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METHODS OF DETERMINING PROTEID NITROGEN IN VEGETABLE MATTER.

BY G. S. FRAPS AND J. A. BIZZELL.

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THE method usually used for the determination of proteid nitrogen, is that modification of the Ritthausen method proposed by A. Stutzer,[1] which consists in precipitating the proteids with copper hydroxide, and determining the nitrogen in the precipitate. This method has been adopted by the Association of Official Agricultural Chemists, and is in use by chemists generally.

Mallet[2] has recently proposed that the proteids be precipitated with phosphotungstic acid at 90° C., using in addition tannic acid when peptones are present.

Wiley[3] determines the proteids in animal materials by precipitating them with bromine.

The work here to be described is a study of the applicability of phosphotungstic acid and bromine as precipitants for the proteids of vegetable materials.

[1] *Jour. f. Landw.*, **28**, 103.
[2] Bull. 54, Division of Chemistry, U. S. Dept. of Agr.
[3] Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

THE PHOSPHOTUNGSTIC ACID METHOD.

The method as proposed by Mallet is, briefly, as follows: The sample is digested with hot water, filtered on a nitrogen-free filter, and washed with hot water containing a little free acid so long as it gives up soluble matter in sensible amount. It is not advisable to use hot water at first when much starch is present. The filtrate is made slightly acid with acetic acid, heated to about 90°, and filtered. To the second filtrate an acidified solution of phosphotungstic acid is added so long as a precipitate continues to be formed, avoiding any large excess of reagent, the liquid heated to about 90°, filtered, and the precipitate washed with water of about the same temperature. The nitrogen in the precipitates is determined by the Gunning-Kjeldahl method, and calculated to proteids. When peptones are present they are precipitated with tannic acid from the solution which has been acidified with acetic acid. When proteoses are present it may be well to make a check determination of their amount by saturation of the aqueous solution, after acidification with acetic acid, heating and subsequent cooling, with zinc sulphate, and determining nitrogen in the precipitate. It may be well to remove fat when it is present in large quantity.

METHOD MODIFIED.

The method above described involves three, or, if peptones are present, four filtrations, which make it very long and tedious. The object of the precipitation with acetic acid is to reduce the bulk of the subsequent phosphotungstic acid precipitate, out of which the amides are to be dissolved by hot water. Its use is unnecessary. When the above method was followed it was found impossible to get a clear filtrate from most of the vegetable materials tested, although various modifications were tried. At 60°, however, no such difficulty was encountered, although at a slightly higher temperature—depending on the material—turbidity would begin to appear. It was also found that between 60° and 100°, a considerable portion of the nitrogen goes into solution. For this reason the temperatures of 60° and 100° were selected for further tests, 100° giving the maximum turbidity and minimum amount of nitrogen, 60° the minimum of

turbidity, *i. e.*, a clear filtrate. The method after much experimentation was simplified as follows: 1.4 grams of the substance in a beaker were stirred well with 100 cc. water, the phosphotungstic acid reagent added and the liquid heated. The liquip was kept at the desired temperature (60° or 100°) for fifteen minutes, filtered, the precipitate washed with water at the same temperature, and nitrogen determined in it.

The reagent used was a 5 per cent. solution of phosphotungstic acid in 2.5 per cent. hydrochloric acid; 5 cc. were used for 3 per cent. or less of nitrogen, 10 cc. for 6 per cent., and 15 cc. for 9 per cent.

EFFECT OF REAGENT.

In dealing with vegetable materials it was found impossible to tell when a slight excess of the phosphotungstic acid reagent had been added. The following results were obtained by using different quantities of the reagent, and heating to 60°. The figures are means of two closely agreeing determinations.

No. 1. COTTONSEED MEAL.

	Nitrogen. Per cent.
10 cc. reagent	6.61
30 " "	6.64
50 " "	6.27

No. 2. WHEAT BRAN.

5 cc. reagent	2.07
10 " "	2.08
25 " "	2.11
45 " "	2.09

No. 3. COWPEA MEAL.

5 cc. reagent	3.18
10 " "	3.11
25 " "	3.22
45 " "	3.17

A small excess of reagent does not affect the results. A very large excess affects them in the case of cottonseed meal. It seems that 5 cc. of the reagent are sufficient for any vegetable material containing less than 3 per cent. of nitrogen, 10 cc. for 6.5 per cent., and 15 cc. for 9 per cent.

EFFECT OF TEMPERATURE.

As has already been stated, a clear filtrate could not, as a rule,

be obtained at a temperature much over 60°, and nitrogen goes into solution between 60° and 100°. In cottonseed meal and wheat bran, the greatest amount of solution takes place between 75° and 90°; cottonseed meal gave at 60°, 6.61 per cent. nitrogen; at 75°, 6.58 per cent.; at 90°, 4.94 per cent.; at 100°, 4.22 per cent. Wheat bran at 60° gave 2.08 per cent. nitrogen; at 75°, 2.01 per cent.; at 100°, 1.75 per cent. The amount of nitrogen dissolved between 60° and 75° is very small.

In order to show the solvent action between 60° and 100°, the following figures are given. Of the nitrogen precipitated at 60°, in cottonseed meal (No. 1.), 36 per cent. goes into solution at 100°; another sample (No. 2.), 24 per cent.; still another (No. 3.), 21 per cent.; cowpea meal, 9 per cent.; green peas, 7 per cent.; soy beans, 18 per cent.; horn meal, 9 per cent.; linseed meal, 12 per cent.; and dried blood, 47 per cent.

Working with blood at 100°, it was found that 5.97 per cent. (37.31 per cent. proteids) goes into solution between 60° and 100°. This sample of blood contained 13.66 per cent. nitrogen, 13.39 per cent. of it being insoluble in water. The filtrate from 100° phosphotungstic acid method was clear, and remained clear although 5.97 per cent. of proteid nitrogen was therein dissolved. This observation threw doubt upon the basis upon which the phosphotungstic acid method is founded; namely, that the phosphotungstic acid precipitate with proteids is not soluble in hot water. This statement is based upon the observation that "the supernatant liquid remained clear on being heated along with the precipitate and subsequently cooled". The following experiments confirmed this suspicion, and proved that phosphotungstic acid does not completely precipitate proteids at 90° or 100°.

0.35 gram of the materials named below were placed in a Kjeldahl flask, 100 cc.of water and 5 cc. of the phosphotungstic acid reagent added, and the solution heated to 60°. The solution was kept at this temperature for fifteen minutes, filtered, washed with water at the same temperature, and nitrogen determined in the precipitate by the Gunning method. Determinations were also conducted at 90° and 100°. Those at 90° were conducted as the others except that the filtration was proceeded with as soon as that temperature was attained.

Name of material.	Total nitrogen. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.	Nitrogen. 90° phosphotungstic acid method. Per cent.	Nitrogen. 100° phosphotungstic acid method. Per cent.
Casein	14.12	14.24	13.24	13.34
Blood albumen	11.82	11.74	11.26	9.92
Egg albumen	12.42	12.58	12.38	11.90
Haemoglobin	13.40	12.82	11.28	9.20
Blood fibrin	13.94	13.62	....	12.60
Gelatin	14.98	....	12.90	11.52

It will be noted that in every case the proteid precipitate was partially dissolved when it was heated. The phosphotungstic acid reagent therefore is of no value for precipitating proteids at 90° or 100°. At 60°—excepting gelatin, and perhaps haemoglobin,—the proteids seem to be completely precipitated.

COMPARISON OF THE MODIFIED PHOSPHOTUNGSTIC ACID AND THE STUTZER METHODS.

The 60° phosphotungstic acid method has already been described. The following table contains some results obtained by this method together with determinations made by the Stutzer method. The figures are means of two determinations:

Name of material.	Total nitrogen. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.	Nitrogen. Stutzer method. Per cent.
Wheat bran	2.20	2.07	1.79
Corn bran	1.54	1.48	1.38
Waste rape	3.57	2.32	2.62
Green peas	1.76	1.57	1.45
Linseed meal	2.86	2.74	2.62
Cottonseed meal No. I	6.80	6.61	6.51
" " No. II	6.18	6.24	6.17
" " No. III	6.62	6.48	6.42
Dried blood	13.66	12.82	13.00
Soy beans	6.13	5.90	5.97
Horn meal	14.70	13.50	13.00
Cowpea meal	3.32	3.18	3.19

It will be noted that this method gives results which are, as a rule, almost identical with those by the Stutzer method, although slightly higher. The mean difference is +0.06 per cent., with a maximum of +0.50 per cent., and a minimum of —0.30 per cent. Neither method gives good results with blood; the filtrate from blood by the 60° phosphotungstic acid method

contained 0.57 per cent. water-insoluble nitrogen, and gave a reaction (with copper sulphate and caustic soda) for proteids, and the copper hydroxide dissolved 0.39 per cent. of water-insoluble protein. With regard to the other materials it is impossible to say which method is correct. The 60° method promises, however, to be of value. It is possible that the determination might be carried on at a slightly higher temperature than this, but hardly over 80° in any case.

PRECIPITATION WITH ZINC SULPHATE.

A comparison was made between the nitrogen precipitated by zinc sulphate and that by the other methods on a few materials. The method was as follows: 1.4 grams of the substance were heated with 100 cc. of water to boiling, allowed to cool, 2 cc. of dilute sulphuric acid (1:4) and 140 grams crystallized zinc sulphate added. It was allowed to stand a day or more, with frequent stirring, filtered, and washed with a saturated solution of zinc sulphate containing 1 cc. of the dilute acid in 50 cc.

Name of material.	Nitrogen insoluble in zinc sulphate.	Nitrogen. Stutzer method.	Nitrogen. 60° phosphotungstic acid method.
	Per cent.	Per cent.	Per cent.
Cottonseed meal	6.45	6.51	6.61
Soy beans	6.07	5.97	5.90
Blood	13.48	13.00	12.82
Cowpea meal	3.26	3.19	3.18

The results are higher than by the other methods in three of the four cases, and seem to point to the Stutzer method as being more nearly correct.

EXTRACTION OF WATER-SOLUBLE NITROGEN.

Extraction of a vegetable material with hot water sometimes gives discordant results, as was the case with cottonseed meal. The extraction was performed as follows: 1.4 grams were placed in a beaker with 50 cc. water, stirred well, and allowed to stand one hour. The liquid was decanted through a filter, 50 cc. water added to the residue in the beaker, heated to boiling, filtered, and the residue washed with boiling water. The undissolved nitrogen was, in case (*a*) 4.54 and 4.68 per cent., mean 4.61 per cent.; in case (*b*) (6 months later) 4.12 and 4.22 per cent., mean 4.17 per cent.; and case (*c*) (volume of filtrate

less than in case (*b*)) 5.55 and 5.67 per cent., mean 5.61 per cent. There is thus a variation of 1.44 per cent. of nitrogen, or 9 per cent. of protein. It is quite possible that had the extracting water been slightly acid the results would have been more uniform.

THE BROMINE METHOD.

Rideal and Stewart[1] have proposed to use bromine as a precipitant for gelatin. Allen and Searle[2] applied the method to the analysis of meat extracts. Wiley[3] has proposed the following method for the determination of proteids in animal matters. About 1 gram of the dried animal matter is washed with ether by decantation, using from 50 cc. to 100 cc. ether, and decanting through a filter which is to receive the portion insoluble in hot water. After allowing the ether to evaporate, the sample is washed by decantation, first with cold water and then with hot water, the total filtrate being from 300 cc. to 400 cc. The undissolved residues are brought on the filter with the last portions of water and the nitrogen in the residues determined by the Gunning-Kjeldahl method. The filtrate from the insoluble portions is received in Kjeldahl flasks, acidulated with 2 or 3 drops of strong hydrochloric acid, and then about 2 cc. of liquid bromine are added, and the contents of the flask shaken vigorously. Bromine is added until about 0.5 cc. remains undissolved and the supernatant liquid is thoroughly saturated. After standing over night, it is filtered and washed by decantation, the globule of bromine serving to saturate the wash-water. The filter with the precipitate is returned to the flask in which precipitation has taken place, and the nitrogen therein determined by the Gunning method.

METHOD MODIFIED.

After some experimentation the method above described was modified for vegetable materials as follows: 200 cc. of water were added to 1.4 grams of the substance in a Kjeldahl flask, heated to boiling, and allowed to cool. It was then acidified with hydrochloric acid, and bromine added until a small globule remained undissolved, the liquid allowed to stand over night,

[1] *Analyst*, 22, 228.
[2] *Ibid.*, 22, 258.
[3] Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

filtered, and the precipitate washed by decantation, keeping the wash-water saturated with bromine. The filter and precipitate were returned to the flask, and the nitrogen therein determined by the Kjeldahl method.

COMPARISON OF THE BROMINE AND STUTZER METHOD.

Proteid nitrogen was determined in a number of materials by the method just described, and the results compared with those obtained by the Stutzer method. The following table contains the results:

Name of material.	Nitrogen. Stutzer method. Per cent.	Nitrogen. Bromine method. Per cent.
Corn silage	0.68	0.67
Crabgrass hay	1.38	1.51
Green peas	1.45	1.25
Cattail millet	1.34	1.10
Linseed meal	2.62	2.37
Corn bran	1.38	1.11
Wheat bran	1.79	1.51
Dried blood	13.00	12.53
Cowpea meal	3.19	2.53
Sheep excrement	2.79	2.13
Soy beans	5.97	5.23
Green rape	2.62	1.84

The bromine method is not applicable in the case of cottonseed meal. In one case the meal was extracted with water, and the extract gave a precipitate which settled almost immediately and contained 0.51 per cent. nitrogen. A duplicate determination gave a turbid liquid, which would not filter clear after standing over night, and when the precipitate finally settled it yielded only 0.10 per cent. nitrogen. When the meal was treated directly with bromine a turbid liquid was formed which refused to filter clear and the precipitate contained varying amounts of nitrogen. The results by the bromine method with two exceptions, are lower than with the Stutzer or the phosphotungstic acid methods. Until it has been proved that bromine precipitates all vegetable proteids quantitatively, which is doubtful, this method must be condemned.

THE STUTZER METHOD.

The Stutzer method used in this work is as follows: place 0.7

gram of the substance in a beaker, add 100 cc. water, heat to boiling, or, in case of substances rich in starch, heat on the water-bath ten minutes; add a quantity of copper hydroxide mixture containing about 0.5 gram of the hydroxide; stir thoroughly, filter when cold, wash with cold water and without removing the precipitate from the filter, determine nitrogen adding sufficient potassium sulphide solution to completely precipitate all copper and mercury. If the substance examined consists of seeds, or seed residues, or anything else rich in alkaline phosphates, add a few cubic centimeters of a concentrated solution of alum before adding the copper hydroxide and mix well by stirring.

Several objections have been made to this method. It has been stated[1] that, in some cases, working with a proteid alone, the copper compound underwent partial solution, a blue liquid being formed, although care had been taken to avoid the presence of free alkali. The proteids acting in this way were not named. Another objection has been founded on "the very slight solubility of the copper salts of some of the simpler amido-acids, especially leucin and glutamic acid; in a less degree the same statement applies to aspartic acid. Even at the temperature of boiling water the copper compounds of these substances are but very sparingly soluble, and if the liquid after digestion with cupric hydroxide, be filtered cold,[2] the compounds in question will, if present, be almost certainly left on the filter along with the proteid material."

Laszczynski[3] also states that copper hydroxide precipitates the albumen of wort and beer completely, but also partly precipitates the albumoses and amides.

The copper salt of leucin is soluble in 3,045 parts of cold water and 1,460 parts of boiling water (Beilstein). When 0.7 gram of the substance and 100 cc. of water are used, for any of this salt to remain on the filter, 0.033 gram must be present, or 0.026 gram of leucin (since it contains 19.5 per cent. copper) which would be 3.7 per cent. The copper salt of glutamic acid is soluble in 3,400 parts of cold water and 400 parts of boiling water, and 0.029 gram must be present before any will separate

[1] Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.
[2] Bulletin 46, Division of Chemistry, U. S. Dept. of Agr. (1895), p. 25.
[3] *Analyst* (Abs.), **24**, 184.

from 100 cc. water, equal to 0.022 gram glutamic acid, or 3.1 per cent. The solvent action of wash-water is left out of consideration.

When the material contains less than 3.7 per cent. leucin, or 3.1 per cent. of glutamic acid, there is no danger of the amide separating in the cold. But the limits are much higher than these. The solubilities above noted are for the pure salts in pure water. E. Schulze[1] emphasizes the fact that the copper salts of these amides are much more soluble when impurities are present. While the copper salts of aspartic acid and glutamic acid separate quickly from a pure solution, from a mixture of the two they separate very slowly, or not until the liquid has been evaporated.

It is probably better, however, to conduct the determination in a hot solution.

It has also been objected to this method, that albumoses are not precipitated. This objection might be overcome by the use of tannic acid to precipitate them. The tannic acid should be used after the precipitation with copper hydroxide. It is only in rare cases that its use would be necessary. Qualitative tests with tannic acid were made on the filtrates from cottonseed meal, wheat bran, cowpea meal, corn bran, cattail millet, excrement from crabgrass hay, waste rape, excrement from waste rape, and corn silage. A small precipitate was formed in all cases except with cattail millet and corn silage. The precipitate from cowpea meal and corn bran dissolved when the liquid was heated, reappearing on cooling. A repetition of the experiment showed that the precipitate did not always appear with the same material. A determination of nitrogen in the precipitate from cottonseed meal gave 0.03 per cent.—practically none.

CONCLUSIONS.

Phosphotungstic acid does not precipitate proteids completely at 90° or 100°.

Phosphotungstic acid at 60° precipitates very nearly the same quantity of nitrogen (with vegetable materials) as copper hydroxide.

Extraction of proteids with hot water does not always give concordant results.

[1] *Landw. Versuch-Stat.*, 6, 220 (1880).

Bromine is not a suitable precipitant for proteids in vegetable materials.

The Stutzer method seems to be the method open to the fewest objections.

Acknowledgment is due Mr. H. W. Primrose, formerly assistant chemist, for assistance in the analytical work.

The above investigation was carried out in the laboratory of the North Carolina Agricultural Experiment Station with the permission of Professor W. A. Withers, chemist.

DETERMINATION OF CARBON IN FERROCHROME.

By A. A. Blair.

Received August 14, 1900.

THE method in general use for the determination of carbon in ferrochrome may be briefly described as follows: Place 1 gram of the finely ground ferrochrome in a porcelain or platinum boat with 25 grams of fused potassium bisulphate and insert the boat in a porcelain tube in a gas furnace. Fit each end of the tube with a rubber stopper carrying a glass tube, and fill the forward part of the tube with lumps of cupric oxide. Connect the tube in the forward stopper with a U-tube containing strong sulphuric acid and chromic acid, a second U-tube containing dry pumice, a third containing dried, not fused, calcium chloride, the weighed absorption apparatus, and a guard tube. Connect the tube in the rear stopper with sources of purified oxygen and air. Start the oxygen through the apparatus and heat the tube carefully, beginning at the forward end which contains the oxide of copper, until the entire length of the tube inside the furnace is at a dull red heat in order to fuse the contents of the boat. Replace the oxygen with air, detach and weigh the absorption apparatus.

This does not seem very troublesome, but in practice several difficulties arise that make the method not only unsatisfactory, but very unreliable.

The sulphuric acid, both that evolved from the potassium bisulphate as sulphuric acid, and that evolved as sulphurous acid and oxidized to sulphuric acid by the oxide of copper and oxygen, acts on the rubber stoppers and sometimes carbonizes them

sufficiently to give results several times greater than the actual carbon content of the ferrochrome. The spattering of the bisulphate, no matter how carefully the heat is applied, generally covers the inside of the tube around the boat and cements boat and tube together. The absorption of sulphuric acid by the oxide of copper causes the latter to swell, usually breaking the tube in the second, and sometimes while it is cooling, in the first determination.

To avoid these difficulties and sources of error, I have devised the apparatus shown in the cuts.

Fig. 1 shows the platinum boats and cover. The smaller

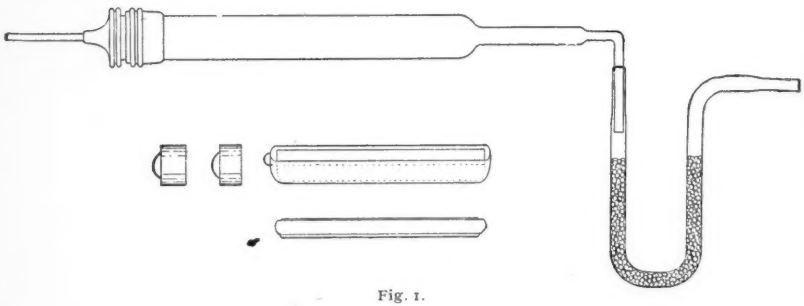

Fig. 1.

boat, 150 mm. long and 25 mm. wide, fits inside the larger and the cover is so arranged that any particles from the melting mass thrown on it run into the larger boat and thus keeps the tube itself perfectly clean.

The platinum tube, shown also in Fig. 1, is 400 mm. long and 30 mm. in diameter and is closed with a ground joint at the rear. The forward end for a distance of 75 mm. is contracted to 12 mm. and filled with platinized asbestos. It is then further contracted to 6 mm. in diameter, and a piece of glass tubing filled with glass beads is fused to it after it is bent downwards at an angle of 90°. The platinized asbestos facilitates the oxidation of the sulphurous acid evolved from the fused mass. The plugs are made of pumice wrapped with platinum foil, and are pushed in after the boat. They serve to fill the back end of the tube and prevent the diffusion of the evolved gases and consequent condensation of sulphuric acid around the ground joint.

Fig. 2 shows the general arrangement of the apparatus. The purifying apparatus for oxygen and air is shown in detail in Fig. 3. The tubes A and B contain respectively potassium hydroxide and concentrated sulphuric acid. It is almost impossible with this form of tube to throw out the contained liquid either forward or backward. In Fig. 2, A is the platinum tube, and B the glass tube containing beads fused to the contracted end of the platinum tube at C. D, D are glass flasks containing a solution of 150 grams of chromic acid and 300 cc. of strong sulphuric acid to the liter. These flasks stand on a copper plate and are heated by a Bunsen burner. The solution serves to oxidize any sulphurous acid that may have escaped oxidation in the contracted part of the platinum tube. E is a U-tube filled with glass beads, and acts as a condenser; F contains pumice saturated with chromic acid, and G contains dried calcium chloride. The absorption apparatus and guard tube follow. The latter is connected by a rubber tube with the gasometer, shown in the cut, which acts as an aspirator and serves to relieve the pressure in the apparatus, which, on account of the condensation of strong sulphuric acid in the tube B and the high spe-

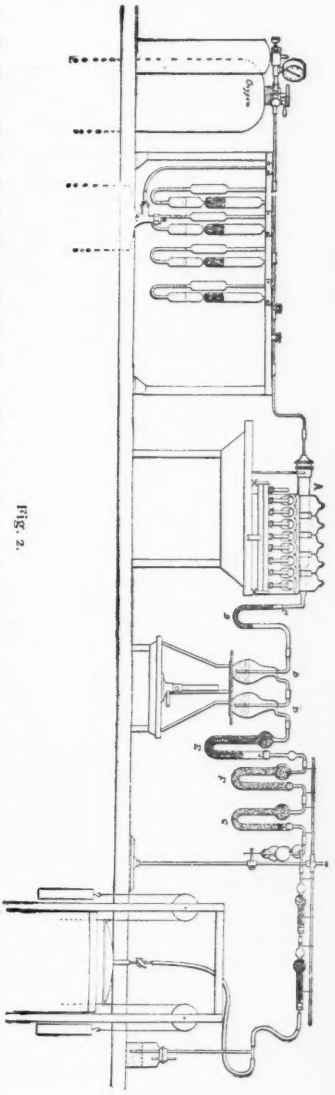

Fig. 2.

cific gravity of the liquid in the flasks D, D, would otherwise be excessive. The details of this connection are shown in Fig. 4.

The method is as follows: Place 25 grams of pure potassium bisulphate in the small boat (Fig. 1), and fuse it over a Bunsen burner or blast-lamp to destroy any carbonaceous matter and allow it to cool. When cold spread 1 gram of the finely ground sample evenly over the surface of the fused mass, place the boat

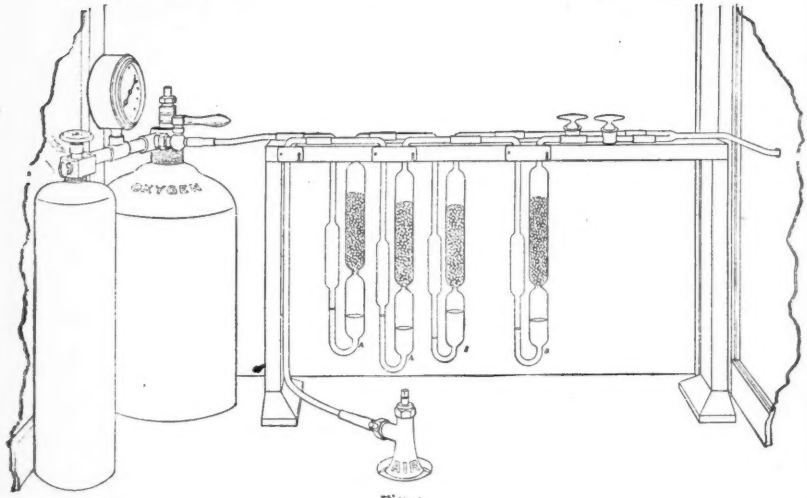

Fig. 3.

inside the larger boat, arrange the cover, place the boats in the tube, insert the plugs and close the tube with the ground joint. Connect the apparatus as shown in Fig. 3, and start a slow current of oxygen through the apparatus. Light the burners under the forward end of the tube which contains the platinized asbestos, and when this is red hot light the burner under the forward end of the boat and light the others successively until the tube is red hot for its entire length where the boat rests. Keep the tube hot for twenty minutes, replace the oxygen with air, turn out the lights, allow the air to run about thirty minutes and detach and weigh the absorption apparatus with the usual precautions.

As a large amount of sulphurous acid is produced it is neces-

sary to heat the tube very gradually in order to keep an excess of oxygen in the tube to oxidize all the sulphurous acid. As the sulphuric anhydride does not condense readily, a slow cur-

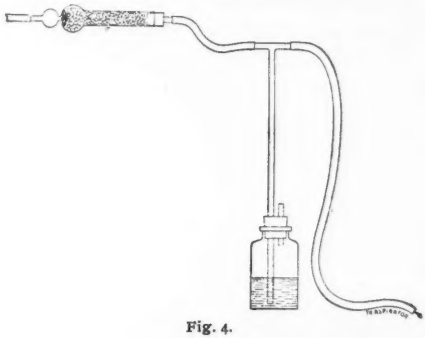

Fig. 4.

rent of gas is requisite, and a combustion requires about two hours and a half.

At the end of the operation the tube is opened and the plugs and boats removed. The fused mass is readily removed from the boats which, with the cover, are washed and ignited, ready for another combustion. About three determinations can be made in a day. Duplicate determinations agree within 0.01 per cent.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 51.]

THE ELECTROLYTIC OXIDATION OF TOLUENE.

BY AARON MERZBACHER AND EDGAR F. SMITH.

Received September 7, 1900.

THE oxidation of toluene by electrolytic oxygen has been tried by Jos. H. James.[1] The products were a minute quantity of liquid, with an ester-like odor, and a resin, together with unaltered toluene.

Our attention has been attracted to this interesting subject and we have repeated the experiments, varying the conditions, of course, with the hope of finally changing the methyl side-chain to carboxyl.

The apparatus used in the electrolysis was similar to that

[1] This Journal, 21, 890.

generally employed in electrolytic oxidations: a large beaker glass in which stood a porous cup containing the anode liquor, and separating it from the cathode liquor. The porous cup was provided with a rubber stopper, carrying a condenser. The cathode liquor was either a 15 per cent. acid or alkali solution Ordinary alcohol served as solvent for the toluene.

Experiment 1.—The conditions were as follows:

Toluene	10 grams.
Concentrated sulphuric acid	5 cc.
Water	50 cc.
Alcohol	150 cc.
$N.D._{100}$	1.1 A.
Volts	3.7
Temperature	40° C.
Time	7 hours.

As the action progressed the liquor assumed a dark yellow color. Upon examination, at the expiration of the oxidation period, unaltered toluene and a little resin were found present.

Experiment 2.—Acetone was substituted for the alcohol and the conditions were:

Toluene	10 grams.
Concentrated sulphuric acid	5 cc.
Water	75 cc.
Acetone	175 cc.
$N.D._{100}$	1.1 A.
Volts	3.5
Temperature	35°
Time	6 hours.

The anode liquor was carefully searched for new products: toluene and a little resin represented all that could be discovered.

Experiment 3.—An alkaline liquor was substituted for the acid of the two preceding experiments. The conditions were:

Toluene	10 grams.
Alcohol	110 cc.
Water	50 cc.
Sodium carbonate	5 grams.
$N.D._{100}$	0.54 A.
Volts	14
Temperature	40° C.
Time	3 hours.

Carbon dioxide was conducted through the cathode liquor

during the experiment. Very little of the toluene was changed. Resin was formed but nothing definite could be extracted from it.

Experiment 4.—A return to an acid solution will be observed in this experiment. Larger quantities of material were also used. The conditions were:

Toluene	55 grams.
Alcohol	190 cc.
Concentrated sulphuric acid	15 cc.
Water	15 cc.
$N.D._{100}$	1.1–1.6 A.
Volts	5–26
Temperature	20°–33° C.
Time	12 hours.

The anode liquor had the odor of benzaldehyde, and apparently that of ethyl benzoate. Three grams of resin were obtained. The fraction, boiling at about 213° C., was saponified with caustic potash, and the solution acidified with hydrochloric acid. The product, which separated, was recrystallized from ether. It melted at 121° C., and showed the characteristic tests of benzoic acid. The oxidation of toluene to benzoic acid had, therefore, really taken place, but in the presence of sulphuric acid and alcohol, ethyl benzoate (b. p. 213°) was formed. The quantity of the latter was not very great. The oxidation was far from being quantitative.

Another fraction, obtained from the anode liquor, boiled at 110°–190°. Phenylhydrazine was added to it. The hydrazone, which separated, was purified, when it melted at 150°, the melting-point of the hydrazone of benzaldehyde.

Additional experiments were made; the products were *resin*, *benzaldehyde*, and *ethyl benzoate*. The tests for the last two bodies were unmistakable. The gases evolved in these oxidations were carbon dioxide and oxygen.

The oxidation of ethyl benzene, under conditions similar to those last mentioned for toluene, gave some resin, ethyl benzoate, benzaldehyde, and a small fraction containing an aldehyde other than the latter, but in such slight amount that it could not be definitely identified.

It is proposed to attempt the electrolytic oxidation of the xylenes and of mesitylene.

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[CONTRIBUTION FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

LECTURE EXPERIMENTS ILLUSTRATING THE ELECTROLYTIC DISSOCIATION THEORY AND THE LAWS OF THE VELOCITY AND EQUILIBRIUM OF CHEMICAL CHANGE.

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INTRODUCTION.

THE experiments to be described in this paper were originally devised as an accompaniment to an extended course of lectures on theoretical chemistry.[1] Most of the principles illustrated are, however, of such fundamental importance that they must soon be generally introduced even into elementary lecture courses on inorganic and analytical chemistry; and it is the hope of the authors that this series of experiments will not only be of assistance to teachers of theoretical chemistry, but will also serve in some degree to hasten and facilitate the introduction of instruction in the principles of chemical equilibrium and of electrolytic dissociation into the elementary courses.

A few lecture experiments of a somewhat similar character have been previously published. Those of Küster,[2] and of Lash Miller and Kenrick,[3] may be specially referred to.

The experiments are presented below in the form believed to be most convenient for those desiring actually to perform them. They are described in great detail, with the hope of saving others the large amount of time which has been expended in the attempt to find the best conditions for rapid and effective lecture demonstrations. It is, nevertheless, true that a slight accidental variation in one of the conditions, such as the dimensions of the apparatus employed, the temperature, or the concentration of the substances, may make modifications necessary; it is, therefore, of course, advisable to try the experiments before the lecture.

[1] Many of these experiments were shown in a lecture on "Some Applications of the Electrolytic Dissociation Theory" given before the American Chemical Society at its Columbus Meeting.

[2] *Ztschr. Electrochem.*, **4**, 105.

[3] This Journal, **22**, 291–300; See also Jones and Allen: *Am. Chem. J.*, **18**, 377; and Stieglitz: *Ibid.*, **23**, 404.

The principles illustrated have been stated as briefly as possible in a non-mathematical form: in spite of the familiarity of these principles, it has seemed desirable to state them explicitly, in order to make clear the exact significance of each experiment.

PART I.—ELECTROLYTIC DISSOCIATION.

EXPERIMENT I.

Principle Illustrated.—The physical properties of dilute aqueous salt solutions are additive, being dependent on the nature of the metal and of the acid component of the salt, but not on their mutual relations. Since most salts in moderately dilute aqueous solution are, according to the dissociation theory, almost completely dissociated into their ions, all properties of such solutions must be the resultant of the properties of the solvent and of the separate ions, each ion having a definite influence which is independent of the nature of the other ion simultaneously present and of that of the undissociated salt from which it originated. This principle is best illustrated in the case where one of the ions has a characteristic property, such as color, not possessed at all by the other ion. Thus, all the salts of a metal whose ion is colored must have the same color in dilute aqueous solution, provided the negative ion of the salt is colorless, however different may be the colors of the undissociated salts. The colors of the latter may be shown, either in the solid state, or in a concentrated alcoholic solution.

Preparation of the Experiment.—Dissolve 60 grams of powdered $CoCl_2.6H_2O$ and 73 grams of $Co(NO_3)_2.6H_2O$ each in 100 cc. of alcohol, thus making a fivefold normal solution of each salt. Dissolve 27 grams of anhydrous cupric chloride (made by heating the blue crystals in a porcelain dish over a free flame) and 48 grams of $Cu(NO_3)_2.3H_2O$, each in 100 cc. of absolute alcohol, thus making a fourfold normal solution of each salt. Pass into the cupric chloride solution a few cubic centimeters of dry hydrochloric acid gas. Place 20 cc. of each of these solutions in four large test-tubes. Provide also distilled water, concentrated ammonia, and 20 cc. of concentrated potassium cyanide solution.

Experiment.—Add 100 cc. of cold water to each of the four solutions. Then add 20 cc. of ammonia to one of the copper

solutions, and 20 cc. of concentrated potassium cyanide solution to one of the cobalt solutions.

Observations.—The alcoholic solutions of cobalt chloride and nitrate are deep violet-blue and purplish red, respectively, but become of the same shade of pink after dilution with water. Those of copper chloride and nitrate are originally greenish black and light blue, respectively, but become of the same shade of blue on dilution. The ammonia added to the copper solution produces a much more intense blue coloration of a different shade, and the potassium cyanide added to the cobalt solution changes its color from pink to brown.

Remarks.—The hydrochloric acid gas is passed into the cupric chloride solution in order to avoid the precipitation of a basic salt on subsequent dilution.

The change in color accompanying the dilution may well be due mainly to hydration of the salts rather than to dissociation of them; but whatever the cause, the experiment evidently still illustrates the principle of the dependence of the properties of dilute aqueous solutions on those of the separate ions. The addition of ammonia to the copper solution transforms the copper ions into complex positive ions of the form $Cu(NH_3)_x$; and that of potassium cyanide to the cobalt solution converts the cobalt ions into complex negative ions, probably of the composition, $Co(CN)_6$. These explanations show that the exceptions to the principle of additivity which are illustrated by the last part of the experiment are in full accord with the dissociation theory; for the nature of the ions having changed, the color of the solution must change likewise.

EXPERIMENT II.

Principle Illustrated.—Metathetical reactions between dissolved salts take place instantaneously, whatever may be the nature of the salts, while those in which organic compounds are involved commonly require an appreciable time which varies greatly with the nature of the compound. This difference of behavior is, according to the dissociation theory, due to the fact that the ions of salts, being already separated by the solvent, are capable of immediate combination, when those which have the tendency to combine are brought into contact, while the component elements

or radicals of organic substances must be separated from each other before they can enter into a metathesis. A very slight degree of dissociation of the salts is sufficient, however, owing to the fact that the ions removed by the metathesis are immediately replaced by others by the spontaneous and almost instantaneous process of dissociation.

Preparation.—Prepare 100 cc. of nearly saturated solution of potassium bromide and of zinc bromide in alcohol, and equal quantities of 5 per cent. solutions of isopropyl bromide, ethyl bromide, and phenyl bromide. Place these solutions in five lecture jars. Prepare 150 cc. of a nearly saturated alcoholic solution of silver nitrate (about 25 grams to the liter). Provide a stirring rod with one end flattened at right angles to the rod, for vertical stirring.

Experiment.—Add 20 cc. of the alcoholic silver nitrate solution to each of the five bromide solutions and stir.

Observations.—The potassium and zinc bromide solutions both give instantly with the silver nitrate a copious flocculent precipitate. The isopropyl bromide solution becomes turbid immediately, but an appreciable time is seen to be required for the completion of the precipitation. The ethyl bromide remains clear for a few seconds, and then becomes turbid, but the turbidity increases very slowly on standing. The phenyl bromide gives no turbidity, even after long standing.

Remarks.—Care must be taken that the ethyl and phenyl bromides are free from hydrobromic acid and bromine. These impurities, if present, may be removed by washing in a separatory funnel, first with dilute sodium carbonate solution, and then with water.

EXPERIMENT III.

Principle Illustrated.—The passage of electricity through a salt solution causes the metallic component of the salt to move in the direction of the current, and the acid component to move in the opposite direction. The products into which salts in aqueous solution are dissociated are therefore electrically charged molecules or ions.

Preparation.—Cut 10 grams of agar-agar in small pieces, place in a casserole, add 500 cc. of cold water, heat to boiling,

and boil until a clear solution is formed. Strain while still hot through a piece of cloth, and preserve the jelly formed on cooling as a stock for use in this and the next two experiments. To 35 cc. of the remelted agar add 8 cc. of saturated cupric chloride solution, a few drops of acetic acid, and 6 cc. of saturated potassium bichromate solution. Pour enough of this solution into a U-tube 2 cm. in diameter and 16 cm. high to fill the tube 3–4 cm. above the bend, and allow the jelly to harden. Sprinkle on each surface a little bone-black to mark the boundary, then pour into each arm a few drops (to fix the bone-black in place) of a solution made by mixing 4 cc. of saturated potassium chloride solution with 15 cc. of the melted stock-agar, cool in water, and after a few moments pour in enough more of this mixture to form a layer a few centimeters high in each arm. After this has hardened, pour into each arm a few cubic centimeters of saturated potassium chloride solution, insert electrodes of platinum wire in both arms, and connect them through an open switch and a 32 candle-power 110-volt lamp with the terminals of a 110-volt direct-current circuit. Place the U-tube in a beaker of water containing a large quantity of ice.

Experiment.—Close the switch and allow the current to pass through the tube for ten to thirty minutes, stopping it temporarily if the agar should show signs of melting.

Observations.—The copper chromate jelly filling the bottom of the tube has a deep green color. After the current has passed for some minutes a blue zone (due to the copper ions) appears above the bone-black boundary in one arm, and a yellow zone (due to chromate ions) above the bone-black in the other arm, and these zones both extend upwards as the electrolysis continues. The zones immediately below the bone-black in both arms also acquire a blue and yellow color respectively, while the central portion beneath remains unchanged in color.

Remarks.—The experiment should be prepared not more than an hour or two before the lecture, as otherwise the boundaries will not be sharp, owing to diffusion. It is desirable to use, as directed, a larger proportion of copper salt than corresponds to the normal chromate, since otherwise the color of the blue copper zone will not be deep enough to be visible at a distance. The

acetic acid is added to prevent the precipitation of a basic chromate. The potassium chloride in the arms of the tube serves to form a colorless conducting layer, its ions carrying the current to and from the boundary of the copper chromate. Accurate experiments have shown that the addition of enough agar to form a solid jelly does not affect the rate of migration of the ions more than a few per cent.; there is, therefore, no objection to its use for purposes of demonstration.

EXPERIMENT IV.

Principle Illustrated.—The rate of migration of the ions is dependent on their nature. The hydrogen ion moves most rapidly, the hydroxyl ion about one-half as fast, and other inorganic ions from one-fourth to one-eighth as fast as the hydrogen ion. The rate of motion of the ions and the number of them present are the two factors determining the conductivity of a solution.

Preparation.—Fill the bend of a U-tube (2 cm. in diameter, and 16 cm. high) and one of its arms up to a point 5 cm. from the top with a jelly made of 16 cc. of saturated potassium chloride solution, 12 drops of phenolphthalein solution, 50 cc. of the stock-agar (see Expt. III), and just enough potassium hydroxide to color it deeply red. Fill the other arm of the tube up to 5 cm. from the top with some of the same jelly to which has been added just twice as much hydrochloric acid as is needed to decolorize it. Place platinum wires in the air spaces at the top of each arm, and connect these wires through a 32-candle-power 110-volt lamp with the terminals of a 110-volt direct-current circuit in such a manner that the current will enter the arm containing the colored jelly. Place the tube in a beaker of water containing pieces of ice. Prepare a mixture of 0.5 cc. of hydrochloric acid (sp. gr. 1.12), 6 cc. of saturated copper chloride, and 20 cc. of water, and a mixture of 2 cc. of 10 per cent. potassium hydroxide solution with 20 cc. of saturated potassium chloride solution.

Experiment.—Nearly fill the arm of the tube containing the colored jelly with the solution of copper chloride and hydrochloric acid and the other arm with the solution of potassium hydroxide

and chloride, close the switch, and allow the current (of about 0.5 ampere) to pass for about fifteen minutes.

Observations.—A colorless zone (due to the hydrogen ions) descends into the pink jelly to a depth of about $5\frac{1}{2}$ cm., and this is followed by a blue zone (due to the copper ions) to a depth of 1 cm. In the other arm a pink zone (due to the hydroxyl ions) descends into the colorless jelly to a depth of about $2\frac{1}{2}$ cm.

EXPERIMENT V.

Principle Illustrated.—The composition of the ions can be determined by migration experiments. Thus in the case of the double cyanide of potassium and silver, the silver can be shown to move against the current, thus proving that it forms a part of the negative ion, which has in fact been shown to have the composition $Ag(CN)_2$.

Preparation.—Charge a U-tube, 2 cm. in diameter and 16 cm. high, not more than an hour or two before the experiment is to be performed, in the manner shown in the accompanying scale drawing, with various jellies, designated I, II, III, and IV. Jelly No. I, is prepared from 30 cc. of the stock-agar (Expt. No. III), 6 cc. of saturated potassium nitrate solution, and 6 cc. of a suspension of washed precipitated zinc sulphide in water; jelly No. II, from 15 cc. of the agar and 4 cc. of saturated potassium nitrate solution; jelly No. III, from 5 cc. of the agar, 1 cc. of saturated potassium nitrate, and 1 cc. of a 3 per cent. silver nitrate solution; and jelly No. IV, from 5 cc. of the agar, 1 cc. of saturated potassium nitrate solution, and 1 cc. of a potassium silver cyanide solution made by adding concentrated potassium cyanide solution, drop by drop, to a 3 per cent. silver nitrate solution until the precipitate first formed redissolves. In charging the tube, pour in each portion of melted jelly through a long-necked funnel to avoid contaminating succeeding portions, and cause each to harden by immersing in cold water before adding the next. Make each of the layers of a thickness corresponding to that shown in the drawing, taking especial care that the layers

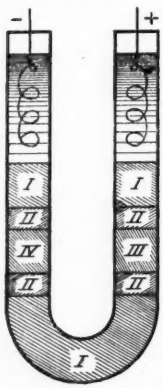


Fig. 1.

of jelly II be not more than 1 cm. thick, since otherwise too long a time will be required for the experiment; and in forming the last layers, pour in first a few drops of the solution, allow this to solidify, and then add the remainder, in order to prevent them from taking up and mixing with any of the jelly beneath. Pour into each arm on top of the jelly some saturated potassium nitrate solution, insert platinum wires, and connect them with the terminals of a 110-volt direct-current circuit in such a manner that the current will enter the arm containing the silver nitrate jelly (No. III). Immerse the tube in a beaker of ice and water.

Experiment.—Cause the current (which will be one of about 0.35 ampere) to pass through the tube for fifteen to twenty minutes, stopping it temporarily or inserting additional resistance if the agar shows signs of melting.

Observations.—The zinc sulphide jelly at the bottom, which is pure white at first, after a few minutes begins to blacken at its surface below the silver nitrate, and a few minutes later at its other surface below the potassium silver cyanide, the blackening extending rapidly downward on both sides. The zinc sulphide layers near the top of the arms remain white throughout the experiment.

Remark.—Zinc sulphide is used instead of an alkaline sulphide to indicate the presence of silver, since, being nearly insoluble, it does not move appreciably with the current.

EXPERIMENT VI.

Principle Illustrated.—The molecular conductivity of salts increases on dilution at first rapidly, and then more slowly, and finally attains a constant maximum value which is not affected by further dilution. The molecular conductivity of a dissolved substance is the conductivity of that volume of its solution which contains 1 mol of the substance, when the solution is placed between parallel electrodes of sufficient extent, 1 cm. apart. According to the dissociation theory, the change of this property on dilution results from the fact that electricity is transported through the solution solely by the ions, and the number of these is increased at the expense of the undissociated portion of the salt by increased dilution, up to the point where the salt is com-

pletely dissociated, after which further dilution has, of course, no further effect.

Preparation.—Construct a high, narrow trough with parallel glass sides and wooden ends and base in the following manner: Cover one of the broad surfaces of each of two strips of wood 45 cm. long, 1 cm. thick, and 2.2 cm. wide, previously oiled and shellaced, with a strip of thin silver foil, attaching this to the wood by means of shellac. Insert these two strips of wood with the silver-covered surfaces towards each other and *uniformly* 18.5 cm. apart between two sheets of plate glass (45 × 22.5 × 0.6 cm.) so as to leave a free space about 1 cm. deep outside of the strips. Clamp the apparatus together temporarily, and fill this free space with a melted cement made by stirring one part of beeswax into five parts of melted rosin. Bind tightly over each of these two ends a piece of stout cloth or canvas, and attach it to the glass sides by means of shellac, so as to hold the whole in position. Insert this cell into a wooden base so made that the cell will fit tightly into a groove to a depth of 1.5 cm.; pour on to the bottom inside more of the above cement heated enough to be very fluid, and allow the cement to cool, so as to form an even horizontal layer. Solder wires to the tops of the silver electrodes. Connect the resistance cell thus constructed in series with a storage cell, a switch, and a suitable current indicator. Use as a current-indicator any Weston station voltmeter, from which the series resistance coil in the back has been removed or short circuited. (The moving coils in all the Weston station voltmeters have a resistance of about 75 ohms; and a full scale deflection is obtained with a current of about 0.012 ampere; the station type is used since it has a pointer which can easily be seen at a distance.) Prepare a stirring rod by closing up one end of a wide glass tube 0.6 meter long. Provide a glass siphon suitable for emptying the resistance cell, and fill it with water; also a funnel attached to a tube long enough to reach the bottom of the cell. Measure out in four graduates three portions of distilled water of 60, 240, and 960 cc., respectively. Prepare 20 cc. of a fourfold normal silver nitrate solution by dissolving 13.5 grams of solid silver nitrate in water, and making the volume up to 20 cc.

Experiment.—Fill the resistance cell with distilled water, and close the switch for a few moments. Insert the siphon, and empty the cell completely, tilting it at the end. Then pour into the bottom of the cell through the funnel the 20 cc. of fourfold normal silver nitrate solution. Close the switch, and note on the board the scale reading. Then pour into the cell the 60 cc. portion of water, stir, and note the reading. Then pour in successively the 240 cc. and the 960 cc. portions of water, noting the readings after the complete addition of each portion.

Observations.—A scarcely noticeable deflection of the needle is produced when the cell is filled with pure water. The scale-readings corresponding to the most concentrated solution and the first fourfold dilution of it are found to differ greatly, those of the first and second dilutions much less, and those of the second and third dilutions by only a relatively small amount; thus the scale-readings in an actual experiment were 7.1, 8.4, 9.2, and 9.5.

Remarks.—In the apparatus and experiment above described the distance between the electrodes, though not 1 cm., is a constant distance, and the amount of the salt used, though not 1 mol, is a definite amount, so that a satisfactory illustration is given of the property of molecular conductivity and of its variation with the dilution, a phenomenon, which, as is well known, was the starting-point of the electrolytic dissociation theory, and one which forms the basis of the most important method of determining dissociation.

The molecular conductivities of the silver nitrate solutions are at the four concentrations, according to Kohlrausch, approximately 39, 63, 80, and 92 units. The effect of having the resistance (about 75 ohms) of the voltmeter constantly in series with the cell is to make the apparent change of conductivity less than the true change; nevertheless, the effect is sufficiently great to make the demonstration an entirely satisfactory one, as is shown by the scale-readings cited above.

If copper electrodes are substituted for the silver ones, and a copper salt solution for the silver nitrate, the change of conductivity with the dilution is still greater; but the experiment is far less satisfactory, for it is not possible, owing to the great dilu-

tion required, to illustrate the approach to a maximum value.

EXPERIMENT VII.

Principle Illustrated.—Different acids of the same concentration differ greatly in their conductivities and degrees of dissociation; but their neutral salts have approximately the same conductivities and same degrees of dissociation.

Preparation.—Fill four 500 cc. bottles with half-normal solutions of hydrochloric acid, sulphuric acid, chloracetic acid, and acetic acid, prepared by weighing out the calculated amounts of the commercial acids. (It is desirable, however, to prove the approximate equivalence in the concentrations of the four acids by titration with normal potassium hydroxide, and to adjust them if they differ by more than five per cent.) Distinctly label these solutions, and reserve them for use in this and later experiments.

Make the apparatus represented in the accompanying figure in the following manner: Procure four glass tubes as nearly alike as possible, of an internal diameter of about 3 cm. and a length of 20 cm. (The straight parts of "student lamp" chimneys can be used for the purpose.) Place in one end of each of these tubes a rubber stopper with one hole in which has been inserted a small glass tube containing a stout copper wire to which a thin circular platinum disk is soldered, this disk covering the small end of the rubber stopper and being attached to it by means of sealing-wax. Set up the tubes in a vertical position with the stoppers at the bottom, holding the tubes in place by means of clamps or by a suitable wooden frame made for the purpose. Insert in the upper end of each of the tubes a rubber stopper carrying a small thick-walled glass tube 22 cm. long through which passes a stout copper wire, to the lower end of which is soldered, at right angles to the wire, a thin circular platinum disk of a diameter a few millimeters less than that of the tube, the disk being reinforced by a thick layer of sealing-wax on its upper surface. These tubes should move freely through the stoppers, but yet be held in place by them. Connect the wire issuing from the bottom of each large tube with a 32-candle-power 110-volt lamp placed in a socket beneath; make also the other connections shown in the drawing, using short coils of

covered flexible wires between the four upper electrodes; and finally, connect through an open switch the upper electrodes with one terminal and the lamps with the other terminal of a

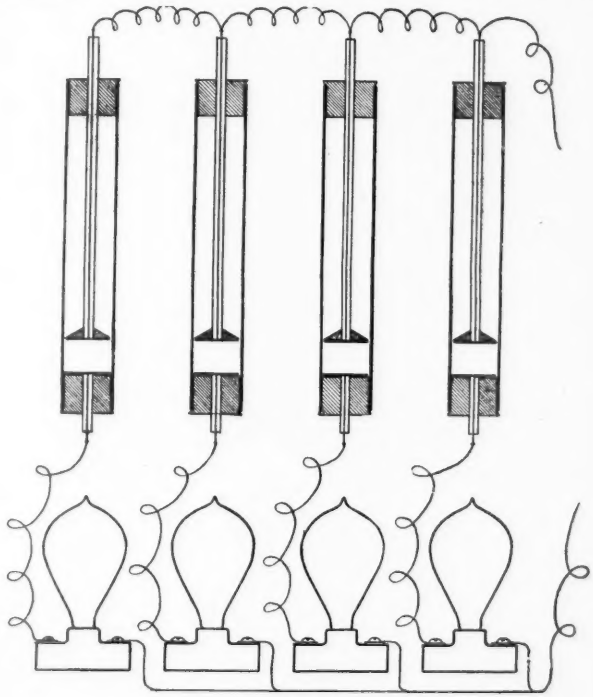


Fig. 2.

110-volt alternating circuit. Place in each tube 120 cc. of distilled water and set the electrodes one-third of the distance from the bottom. Provide a 5 cc. graduated pipette, a little phenolphthalein solution, and 50 cc. of normal potassium hydroxide solution.

Experiment.—Raise the stoppers carrying the upper electrodes, and add to each of the four tubes with the pipette 5 cc. of each of the four half-normal acids, so that they will be in the order, acetic, chloracetic, sulphuric, hydrochloric, and stir thoroughly. Re-insert the electrodes, darken the room somewhat, and close

the circuit. Raise the electrode in the hydrochloric acid solution to the top of the tube, and then adjust the heights of the other three electrodes so that all the lamps beneath glow with equal brilliancy. Admit the light to the room, and call attention to the relative heights of the four electrodes. Then raise the stoppers, and add to each tube two or three drops of phenolphthalein solution and from the pipette about 2.5 cc. of a normal solution of pure potassium hydroxide, adding the last few drops in each case slowly and with vigorous stirring, until the solution remains permanently colored. Again darken the room, set the electrode in the potassium chloride solution about one-third of the total distance from the bottom, and adjust the other three electrodes so that all four lamps glow with equal brilliancy. Admit the light to the room, and call attention to the heights of the four electrodes.

Observations.—Starting as directed with the four electrodes at the same height, about one-third of the distance from the bottom, it is seen when the circuit is closed that the lamps are more brilliant in correspondence with the order, hydrochloric, sulphuric, chloracetic, acetic, the lamp beneath the last-named acid not glowing perceptibly. After the lamps are brought to equal brilliancy by adjusting the electrodes, it is seen that if the upper electrode in the hydrochloric acid is at the top, that in the sulphuric acid is about one-fourth of the distance down, that in the chloracetic acid three-fourths of the distance down, and that in the acetic acid nearly touching the lower electrode. It is seen that nearly equal amounts of potassium hydroxide are required for the neutralization of all four acids, thus proving them of equal concentration. Finally after adjusting the lamps to constant brilliancy, the electrodes in the salt solutions are seen to stand at not far from the same heights.

Remarks.—The chloracetic acid solution must be prepared not more than a few days before it is used, since, otherwise, it will contain an appreciable amount of hydrochloric acid. If an alternating circuit is not available, a direct circuit may be used, but in that case it is desirable that the upper electrodes be made convex downwards so that the gas will escape, and that the circuit be closed only for as short a time as is necessary.

Instead of charging the tubes of the conductivity apparatus during the lecture with the acids, this may be done beforehand, in order to save time; but in that case, the audience is obliged to take for granted the fact that the acids used in the later experiments are identical with those used in this one, a fact which is made obvious if the portions of acids are in each case drawn from the same bottles. In fact, throughout most of the following experiments, much time can be saved in the lecture by measuring out the solutions in advance, the audience being asked to accept the lecturer's statement in regard to their composition. While the purpose of such experiments is to illustrate rather than to demonstrate, it is nevertheless true that they become less satisfactory, the more the audience has to take for granted. To what extent it is desirable to carry the preparation of the experiments, will therefore depend on the character of the lectures, on the time that can be given to experiments, and whether the services of an assistant are available during the lecture.

Lecturers will, we believe, find themselves repaid for the small amount of labor involved in the construction of the apparatus just described; for not only is the above experiment a very satisfactory one, but the same apparatus can be employed for the demonstration of Ostwald's dilution law (see Expt. XII), and for the illustration of the conductivity and dissociation of many substances besides those here used. It should be stated that the apparatus was devised and first constructed by Dr. W. R. Whitney of our Institute.

PART II.—THE VELOCITY OF CHEMICAL REACTIONS.

EXPERIMENT VIII.

Principle Illustrated.—The rate at which a chemical change takes place is proportional to the concentration of each of the substances taking part in it.[1]

Preparation.—In a 2-liter bottle put 1600 cc. of distilled water, 50 cc. of half-normal hydrochloric acid, and 40 cc. of starch solution (made by rubbing 1 gram of potato starch to a paste with

[1] As is well known, the rate is in some cases proportional to that power of the concentration which corresponds to the number of molecules involved; but this experiment illustrates only the simpler case.

5 cc. of cold water, pouring 150 cc. of boiling water over it, allowing the undissolved part to settle, and decanting the supernatant liquid). Prepare a 0.5 normal solution of potassium bromate by dissolving 7 grams of the salt in half a liter of water; also a 0.5 normal solution of potassium iodide by dissolving 42 grams of it in half a liter of water. Reserve these solutions for use in the three following experiments: Provide four 500 cc. white glass stoppered bottles, 8 cm. in diameter, and set two 10 cc. graduates in front of each of them. Prepare a standard blue solution in a fifth 500 cc. bottle by adding to 400 cc. of water, 10 cc. of the starch solution and 1 cc. of a solution of 1 gram of iodine and 2 grams of potassium iodide in 500 cc. of water. Place all five bottles on the lecture table against a background of white paper. Provide a large clock (or stop-watch) with a second hand; also a 500 cc. graduate.

Experiment.—Pour into each of the four bottles from the large graduate 400 cc. of the acid solution in the 2-liter bottle. Pour into the four pairs of 10 cc. graduates respectively 5 cc. of the bromate and 5 cc. of the iodide solution, 10 cc. bromate and 5 cc. iodide, 5 cc. bromate and 10 cc. iodide, and 10 cc. bromate and 10 cc. iodide. Add to each of the four bottles the bromate solution from the graduate before it, and then, at a definite instant, when the second hand of the clock shows an even minute, add simultaneously to the four bottles the measured portions of iodide solution, quickly insert the stoppers, and shake vigorously. Note on the board by reference to the clock the times when each of the solutions becomes of the same shade of blue as the standard, placing the latter in succession by the side of the different reaction bottles.

Observations.—The mixture containing the 10 cc. of both bromate and iodide will become of the same shade of blue as the standard in about thirty seconds. The mixtures with 10 cc. bromate and 5 cc. iodide and with 5 cc. bromate and 10 cc. iodide will both require the same interval of time, which will be about twice as great as that for the first mixture. The mixture containing 5 cc. of both bromate and iodide will require nearly twice as much time as these last mixtures.

EXPERIMENT IX.

Principle Illustrated.—Equal increments of temperature cause an equal multiplication of the velocity of any definite chemical reaction.[1]

Preparation.—Mix in a 2-liter bottle 1100 cc. of water, 100 cc. of 0.5 normal hydrochloric acid, and 30 cc. of starch solution. Put 400 cc. of this solution into each of three 500 cc. white glass-stoppered bottles (8 cm. in diameter); bring by means of suitable baths one of these solutions to 4°, another to 16°, and the third to 28°; and allow the bottles to stand in the baths until the experiment is to be shown. Mix in a 50 cc. graduate 10 cc. of 0.5 normal potassium bromate, 10 cc. of 0.5 normal potassium iodide, and 25 cc. of water, all measured as closely as possible; and pour just 10 cc. of this mixture into each of three 10 cc. graduates. Provide a clock with a second hand, and a large thermometer of short range whose readings are visible at a distance. Prepare in a fourth bottle, just as in Expt. VIII, a blue iodide of starch solution to serve as a standard. Place all four bottles against a background of white paper.

Experiment.—Insert the thermometer in succession in each of the three bottles, and note the temperatures on the board. At a definite instant, when the clock shows an even minute or half minute, pour the three portions of bromate solution into the three bottles, stopper quickly, and shake vigorously. Note on the board the times at which the three solutions reach the same depth of blue as the standard.

Observations.—The times required to reach the color of the standard will be about thirty-two seconds, fifty-eight seconds, and one hundred and five seconds at 28°, 16°, and 4°, respectively.

Remarks.—The hottest solution must not be above 30°, since otherwise a considerable error arises from the lessening of the depth of color of the iodide of starch. Between 4° and 30°, however, the intensity of color undergoes a scarcely perceptible change, as was proved by a special experiment.

EXPERIMENT X.

Principle Illustrated.—The effect of acids in accelerating chem-

[1] This principle may be somewhat more explicitly stated as follows: In the case of any chemical reaction, the velocity-coefficients corresponding to an arithmetical series of temperatures, form a geometrical series.

ical reactions is roughly proportional to their electrical conductivities. The effect is primarily dependent on the hydrogen ions, and is in most cases approximately proportional to their concentration.[1]

Preparation.—Mix in a 2 liter bottle, 40 cc. of 0.5 normal potassium iodide, 40 cc. of 0.5 normal potassium bromate, 40 cc. of starch solution, and 1600 cc. of water. Place on the lecture table the four half-normal solutions used in Expt. VII, four 500 cc. bottles, four 10 cc. graduates, a 500 cc. graduate, and white paper arranged so as to serve as a background.

Experiment.—Measure with the large graduate 400 cc. of the bromate-iodide mixture into each of the four bottles. Pour into the small graduates just 10 cc. of each of the half-normal acids, and place them in front of the four bottles in the order hydrochloric, sulphuric, chloracetic, acetic acid. Add at the same instant the contents of the four graduates to the bottles, stopper quickly, and shake.

Observations.—The solution containing the hydrochloric acid becomes deep blue almost immediately; that with the sulphuric acid, within half a minute; that with the chloracetic acid, after three or four minutes; and that with acetic acid, only after three or four hours.

EXPERIMENT XI.

Principle Illustrated.—Neutral substances sometimes act as powerful catalytic agents.

Preparation.—Place in a liter bottle 800 cc. of water, 40 cc. of 0.5 normal potassium iodide, 40 cc. of 0.5 normal potassium bromate, and 20 cc. of starch solution. Provide a half-normal solution of acetic acid and a neutral saturated solution of ferrous sulphate; also, a graduated 1 cc. pipette, two 500 cc. bottles, and two 50 cc. and one 500 cc. graduates.

Experiment.—Measure into each of the two bottles, with the large graduate, 400 cc. of the bromate-iodide mixture. Measure out in each of the two graduates 50 cc. of the half-normal acetic acid, and add to one of the graduates 0.5 cc. of the ferrous sul-

[1] In the case of the bromate-iodide reaction the accelerating effect increases much more rapidly than the concentration of the hydrogen ions (see *Ztschr. phys. Chem.*, 19, 599); but in spite of this exceptional behavior, it can be used to demonstrate the *order* of the effect of different acids, which is all that is attempted in this experiment.

phate solution. At the same moment add the contents of the graduates to the two bottles, quickly insert the stoppers, and shake.

Observations.—The solution containing the ferrous sulphate becomes deep blue within a few seconds, while that not containing it requires as many minutes to reach the same depth of color.

PART III.—CHEMICAL EQUILIBRIUM OF DISSOCIATED SUBSTANCES.

EXPERIMENT XII.

Principle Illustrated.—The molecular conductivity, and therefore the dissociation, of a slightly dissociated acid varies as the square root of the volume in which a definite quantity of the acid is contained, in accordance with the requirement of the mass action law. The general expression of the effect of dilution on the dissociation of acids, or of the so-called Ostwald's dilution law, is $\frac{d^2}{(1-d)v} = K$, where d is the degree of dissociation, v the volume containing 1 molecule, and K the dissociation-constant. If d is small, the quantity $(1-d)$ can be considered equal to unity without great error, whence the above-stated principle follows.

Preparation.—Place on the lecture table the conductivity apparatus and the half-normal chloracetic acid solution used in Expt. VII. Provide two 300 cc. beakers and a 50 cc. and a 200 cc. graduate, also half a liter of distilled water and have this at the same temperature (that of the room) as the chloracetic acid. Connect the conductivity apparatus through a switch with the terminals of a 110-volt alternating circuit.

Experiment.—Mix in a beaker 50 cc. of the half-normal chloracetic acid solution with 150 cc. of water. In a second beaker dilute 50 cc. of the solution so obtained with 150 cc. of water. Nearly fill three of the tubes of the conductivity apparatus with the half-normal chloracetic acid from the bottle, and with the two diluted solutions in the beakers, respectively. Raise the electrode in the tube containing the most concentrated acid to the top, darken the room, close the circuit, and adjust the other two electrodes so that the three lamps beneath glow with equal brilliancy.

Open the circuit, admit the light, and call attention to the position of the electrodes.

Observations.—At the close of the experiment it is seen that the electrodes in the half-normal solution are about twice as far apart as those in the eighth-normal solution, and about four times as far apart as those in the 1/32-normal.

Remarks.—The remark on Expt. VII in regard to the use of a direct current applies here also.

The distances between the electrodes are directly proportional to the specific conductivities of the solutions; consequently, the molecular conductivities are proportional to the products of these distances into the volumes in which a definite amount of acid is contained.

Chloracetic acid is 5.4, 10.5, and 20.0 per cent. dissociated in 1/2, 1/8, and 1/32-normal solutions respectively. Owing to the rather large degree of dissociation, the proportionality between this and the square root of the volume is not exact; but the deviations are not great enough to be noticeable in the experiment here described.

EXPERIMENT XIII.

Principle Illustrated.—The dissociation of a slightly dissociated acid (or base) is very greatly reduced by the addition of an equivalent quantity of one of its neutral salts. For, according to the mass action law, the product of the concentrations of the two ions of the acid is proportional to the concentration of its undissociated portion, and since the concentration of the negative ion is largely increased by the addition of the neutral salt, the ratio of the concentration of the hydrogen ion to that of the undissociated acid must decrease in the same proportion. In the following experiment, in order to show the difference in the concentrations of the hydrogen ion in the two cases, use is made of the relative effects of the acid, in the absence and presence of its neutral salt, in accelerating the bromate-iodide reaction.

Preparation.—In a liter bottle place 700 cc. of distilled water, 20 cc. of 0.5-normal potassium bromate, 20 cc. of 0.5-normal potassium iodide, and 10 cc. of starch solution. Place on the lecture table the half-normal solution of chloracetic acid and a normal one of potassium hydroxide; also a 500 cc. graduate,

two 100 cc. graduates, a 200 cc. beaker, two 500 cc. bottles, a phenolphthalein solution, and some distilled water.

Experiment.—Measure with the large graduate, 350 cc. of the bromate-iodide mixture into each of the 500 cc. bottles. Measure out 40 cc. of chloracetic acid into each of the two 100 cc. graduates. To one graduate add 60 cc. of water, and mix by stoppering the graduate and shaking. Pour the contents of the other graduate into the beaker, add a few drops of phenolphthalein and about 20 cc. of the normal potassium hydroxide solution, adding the last portion slowly with stirring so as to attain closely the neutral point; then add 40 cc. more of the chloracetic acid solution and pour the mixture back into the graduate. At the same moment add the contents of the two graduates to the two bottles containing the bromate-iodide mixture, insert the stoppers, and shake vigorously.

Observations.—The blue color appears very quickly in the bottle to which only the chloracetic acid was added, but much more slowly in that containing also the neutral salt.

Remark.—The same principle is further illustrated in connection with the two following experiments.

EXPERIMENT XIV.

Principle Illustrated.—The extent to which a weak acid is displaced from one of its neutral salts by another acid added to its solution increases with the degree of dissociation of the added acid. For the displacement depends on the fact that the negative ions of the salt and the hydrogen ions of the added acid when brought together unite in part to form undissociated acid, and the quantity of this which forms is, according to the mass action law, greater, the greater the concentration of the hydrogen ions and therefore the greater the dissociation of the added acid.

Preparation.—Dissolve 6 grams of commercial crystallized alloxan and 2 grams of hydroxylamine hydrochlorate in 200 cc. of water, heat for an hour on a water-bath, and exactly neutralize the solution of violuric acid so prepared with dilute potassium hydroxide solution, with the help of litmus paper, rinsing off the pieces of paper with water after their immersion in the solution, so as to make the color of the litmus evident. (About

55 cc. of a normal solution are required.) Dilute with enough water to make the volume 450 cc. Measure six 50 cc. portions of this solution into six lecture test-tubes 3 cm. in diameter, placed in a rack provided with a background of white paper. Determine accurately the amount of half-normal hydrochloric acid which suffices to decolorize one of these portions to such an extent that it appears of a pale, but distinctly recognizable, pink shade. (Roughly 6 cc. will be required. The exact quantity required is designated M cc. below.) Then entirely decolorize this portion by adding a few more drops of acid. Provide a 10 cc. graduated pipette, an additional lecture test-tube, the four half-normal acid solutions used in Expt. VII, a normal potassium hydroxide solution, a phenolphthalein solution, and a 10 cc. graduate containing a chloracetate solution made by nearly but not quite neutralizing M cc. of the half-normal chloracetic acid with normal potassium hydroxide and diluting up to 10 cc.

Experiment.—Add potassium hydroxide solution in excess to the colorless violuric acid solution, and remove the tube from the rack. Add by means of the 10 cc. graduated pipette to one of the tubes of sodium violurate M cc. of water to serve as a standard and to the four other tubes M cc. of the four half-normal acids in the order acetic, chloracetic, sulphuric, and hydrochloric. Pour one-half of the portion to which the chloracetic acid has been added into the empty test-tube; and add to this 10 cc. of water; and to the half in the original tube add the 10 cc. of chloracetate solution previously prepared after adding to the latter a drop of phenolphthalein solution (to show that it is not alkaline).

Observations.—The colorless violuric acid solution becomes a deep violet when the potassium hydroxide is added. The acetic acid reduces the color to about one-half, and the chloracetic acid to about one-tenth that of the standard; the sulphuric acid gives rise to a pale pink, which, however, is considerably deeper than that produced by the hydrochloric acid. The color of the portion to which both the chloracetic acid and the chloracetate are added is about twice as intense as that of the portion which contains only the chloracetic acid.

Remarks.—The purpose of the addition of potassium hy-

droxide at the start is to illustrate the facts on which the demonstration of the main principle depends, namely that violuric acid in solution is nearly colorless and that its salt is of a deep violet color. The last part of the experiment on the effect of the neutral salt is a further illustration of the principle here under consideration as well as of that underlying Expt. XIII.

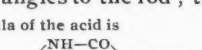
Violuric acid[1] is an acid of about the same strength as acetic acid, the dissociation constants of the two acids being 0.0027[2] and 0.0018, respectively; consequently, the base divides itself nearly equally between the two acids when, as in the experiment, equivalent quantities of them are simultaneously present. Violuric acid is so very much weaker than sulphuric and hydrochloric acids that it is almost completely displaced by both of them; and, to make evident a difference in their behavior, it is necessary to avoid adding enough hydrochloric acid to cause complete decolorization, and to measure quite accurately the amounts of the two acids added; for 10 per cent. excess of the sulphuric acid entirely obscures the difference in their behavior.

EXPERIMENT XV.

Principle Illustrated.—The behavior of indicators used in titrating acids and alkalies is primarily determined by the principles governing the displacement of one acid (or base) from its salt by another. It depends on the relative degree of dissociation of the indicator, which must itself be a very slightly dissociated acid or base, and of the titrated acid (or base.) The behavior of indicators is in some cases also greatly influenced by the phenomenon of hydrolysis. The behavior of di- and tri-basic acids is dependent on the different degrees of dissociation of the acid with respect to its first and second, or first, second, and third hydrogen atoms. More specific explanations follow the experiments described below.

Preparation.—Place 250 cc. of distilled water in each of ten lecture jars of 400 cc. capacity. Provide the following apparatus and solutions: four 50 cc. graduates; several stirring rods with one end flattened at right angles to the rod; two pipettes with rubber

[1] The constitutional formula of the acid is



[2] Magnanini: *Ztschr. phys. Chem.*, **12**, 58.

nipples for dropping; half-normal solutions of hydrochloric acid and acetic acid, and normal solutions of potassium hydroxide, ammonium hydroxide, sodium acetate, sodium carbonate, and phosphoric acid (made by diluting 12 cc. of sirupy phosphoric acid of 1.34 specific gravity up to 500 cc.); and solutions of phenolphthalein and methyl orange as ordinarily prepared for volumetric analysis.

Experiment.—1. Add from the dropping pipette, to each of four of the lecture jars containing water 3 drops of the normal potassium hydroxide solution. To the first and third of these jars add five drops of phenolphthalein and to the second and fourth add five drops of methyl orange. Then add from the pipette, drop by drop, half-normal hydrochloric acid to the first and second jars, and half-normal acetic acid to the third and fourth jars with constant stirring, until the indicator becomes decolorized or changes color. In the case of the fourth jar, after showing that the first few drops cause no change in color, add the acetic acid in larger quantities from a graduate until about 40 cc. have been added. Then add 25 cc. of normal sodium acetate to both the third and fourth jars.

2. To the fifth jar add just 50 cc. of half-normal hydrochloric acid and five drops of methyl orange. To the sixth jar add the same amount of the hydrochloric acid and two drops of phenolphthalein. Add to each jar from a 50 cc. graduate normal ammonium hydroxide, rapidly until 23–24 cc. are added, and then more slowly until the (sharp) end-point is reached in the fifth jar when about 25 cc. have been added, and until the solution becomes of a decided red color in the sixth jar, requiring about 40 cc. Then add ten drops more of phenolphthalein to the latter.

3. Add to the seventh and eighth jars 25 cc. of normal sodium carbonate, and to the former, five drops of methyl orange, and to the latter, five drops of phenolphthalein. Titrate roughly to an end-point with normal hydrochloric acid, adding from a graduate about 50 cc. to the seventh jar and 25 cc. to the eighth.

4. Add to the ninth and tenth jars 50 cc. of normal phosphoric acid and to the former jar five drops of methyl orange and to the latter five drops of phenolphthalein. Titrate roughly to an end-

point with normal potassium hydroxide, adding from a graduate about 17 cc. to the ninth jar and about 34 cc. to the tenth.

Observations and Explanations.—1. The end-point is sharp and requires for its attainment the same quantity of acid whether hydrochloric acid with phenolphthalein, hydrochloric acid with methyl orange, or acetic acid with phenolphthalein, is used; but when acetic acid and methyl orange are employed, the change of color is very gradual and requires a much larger quantity of acid. These results are explained as follows: hydrochloric acid is so much stronger (*i. e.*, more dissociated) than either phenolphthalein or methyl orange, and acetic acid is so much stronger than phenolphthalein, that the indicator is completely displaced from its potassium salt by even an inappreciable excess of the acid; on the other hand, since methyl orange is a relatively strong indicator-acid[1] and acetic acid a relatively weak acid, a large excess of the latter, whereby a considerable concentration of the hydrogen ions results, is necessary in order to displace the indicator completely from its salt. The sodium acetate added at the close of this experiment causes the yellow color of the methyl orange salt to reappear, owing to the great reduction of the dissociation of the acetic acid, whereby it loses its power of displacing the indicator from its salt; this reduction by the sodium acetate is, however, not sufficient to cause any apparent change in the phenolphthalein equilibrium.

2. In titrating hydrochloric acid with ammonium hydroxide, the end-point is sharp when methyl orange is used, while the change to a pink color is very gradual when phenolphthalein is employed. The remarkable behavior of this last indicator is due to the fact that it is such a very weak acid that when the base also is weak, as is the case with ammonium hydroxide, the salt resulting from their union is so readily decomposed by water that an appreciable quantity of it does not form until the ammonium hydroxide is present in considerable excess; on the other hand, methyl orange is so strong an acid that its salts even with weak bases like ammonium hydroxide are not much hydrolyzed. The addition of more phenolphthalein at the end of the exper-

[1] Other hypotheses in regard to the behavior of this indicator have been proposed by Küster (*Ztschr. anorg. Chem.*, 13, 136) and Waddell (*J. Phys. Chem.*, 2, 171); but these lack experimental verification.

iment intensifies the red color; for it causes, just as the excess of ammonium hydroxide does, a decrease in the amount of hydrolysis.

3. The results observed in this experiment are indicated in the description of it. They are explained as follows: the acid ion HCO_3, which begins to form on the first addition of hydrochloric acid, is less dissociated than either of the two indicator acids and consequently does not displace either of them from its salts. When a little more than one equivalent of acid has been added, however, the acid H_2CO_3 begins to form, and since its dissociation is greater than that of phenolphthalein but less than that of methyl orange, it displaces the former, giving an end-point, but does not displace the latter.

4. The results are indicated above. They are readily explained with the help of the following assumptions: The acid H_3PO_4 is a stronger acid than either of the indicators; the ion H_2PO_4 is a stronger acid than phenolphthalein, but a weaker one than methyl orange; and the ion HPO_4 is a weaker acid than either of the two indicators.

EXPERIMENT XVI.

Principle Illustrated.—The product of the concentrations of the ions of a salt with which a solution is saturated (the so-called solubility-product) has the same value whether or not other substances are simultaneously present. The presence of a second salt with a common ion therefore reduces the solubility in accordance with this principle; and two different salts, one having in common the positive ion and the other the negative ion of the salt saturating the solution, must have the same effect in reducing the solubility, assuming, as is usually approximately true, that the two salts are equally dissociated.

Preparation of the Experiment.—Prepare 500 cc. of a saturated solution of silver acetate by shaking an excess of the solid salt with warm water, cooling, and filtering or decanting. Place 200 cc. of this solution in each of two 400 cc. lecture jars. Place in graduates 5 cc. of fourfold normal solutions of sodium acetate and of silver nitrate; also provide a stirring rod.

Experiment.—Add the measured portion of sodium acetate to

one jar and that of silver nitrate to the other jar of the silver acetate solution, and stir vigorously for a few moments.

Observations.—A feathery crystalline precipitate of the same character and amount is produced in each jar.

EXPERIMENT XVII.

Principle Illustrated.—The solubility of a salt in water is increased by the addition of a second salt with different ions when there can be produced by metathesis an undissociated substance; and the increase is greater, the greater the amount of this substance formed. Thus, if to saturated solutions of a salt of a partially dissociated acid are added other acids of varying degrees of dissociation, the increase of solubility caused by these will be greater, the greater the degree of their dissociation; for the amount of undissociated acid produced by the metathesis will increase with the increase in the concentration of the hydrogen ions. The formation of the undissociated substance increases the solubility by decreasing the concentration of one of the two ions of the salt saturating the solution, thus making it necessary for more of the salt to dissolve in order to reproduce the original value of the solubility-product.

Preparation.—Treat 10 grams of salicylic acid with a solution of 3 grams of anhydrous sodium carbonate in 100 cc. of water; filter; boil to expel carbon dioxide; add a solution of 9 grams of silver nitrate in 100 cc. of water; and wash and dry the precipitate. Place about 1 gram of it and 45 cc. of water in each of four 50 cc. wide-mouthed, glass-stoppered bottles. Place in each of four lecture jars 10 cc. of hydrochloric acid of 1.12 sp. gr. and 250 cc. of distilled water. Place on the lecture table also the half-normal solutions of sulphuric, chloracetic, and acetic acids used in Expt. VII; a 5 cc. graduated pipette; a stirring rod; four 25 or 50 cc. graduates with a funnel containing a ribbed filter resting in the top of each.

Experiment.—Add, with the help of the graduated pipette, 5 cc. of the three half-normal acids to three of the bottles containing the silver salicylate. Shake all four bottles vigorously for half a minute and pour their contents on to the four ribbed filters. Allow 25 cc. to collect in each graduate and pour the four

25 cc. portions into the four jars of dilute hydrochloric acid in the order, water, acetic acid, chloracetic acid, and sulphuric acid.

Observations.—The jars to which the water solution and the acetic acid solution are added show a very slight and nearly equal turbidity. The turbidity is much greater in the case of the chloracetic acid, and again much greater in the case of the sulphuric acid.

ON THE PREPARATION OF TRIPHENYLCHLORMETHANE.

BY M. GOMBERG.

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IT is generally stated in smaller as well as in larger[1] text-books on organic chemistry, that when carbon tetrachloride is treated with benzene and aluminum chloride triphenylchlormethane is the principal product of the reaction. This statement is entirely erroneous.

Friedel and Crafts, who were the first to study this reaction, reported[2] that they obtained in this way tetraphenylmethane. E. and O. Fischer[3] were unable to verify this result, but could obtain only triphenylmethane. It is to be presumed that they carried on this reaction in a manner analogous to that followed in the preparation of triphenylmethane from chloroform, *i. e.*, the resulting products, after being freed from the chloride of aluminum and the excess of benzene, were subjected to fractional distillation at the high temperature of 200°–360° C. Later, Friedel and Crafts[4] found that the results vary according to the manner of procedure. On distilling the crude products at a high temperature they also obtained triphenylmethane and thus confirmed E. and O. Fischer's results. But if the entire mixture as obtained by the action of aluminum chloride and benzene upon carbon tetrachloride is at once treated with water, it furnishes large quantities of triphenylcarbinol. From this they concluded that the reaction results principally in the formation of triphenylchlormethane, $(C_6H_5)_3C.Cl$, and this on treatment with water furnishes the corresponding carbinol. They confirmed this

[1] Beilstein: Handbuch, II, 287 (3rd edition).
[2] *Compt. rend.*, 1453 (1877).
[3] *Ann. Chem.* (Liebig), **194**, 254.
[4] *Ann. chim. phys.*, I, 497 (1884).

conclusion by the conversion of the crude chloride into the ethoxy compound:

$$(C_6H_5)_3C.Cl + HOC_2H_5 = (C_6H_5)_3C.OC_2H_5 + HCl.$$

Triphenylmethane is therefore not the first product of the action of benzene upon carbon tetrachloride, but is one of the decomposition products of triphenylchlormethane, formed when the latter is subjected to high heat. That this is likely to occur had been previously shown by E. and O. Fischer on the pure chloro-compound.[1]

Of others who have employed Friedel and Crafts' reaction upon carbon tetrachloride itself or upon its phenylated derivatives may be mentioned Doebner and Magati,[2] Schwartz,[3] Weisse,[4] and V. Meyer.[5] They all report the formation of triphenylmethane,—due, no doubt, in every instance to the subsequent decomposition of the triphenylchlormethane. In this connection, Nencki and Meissel's work may be mentioned. Nencki[6] has shown that ferric chloride may with advantage be substituted for aluminum chloride in many syntheses where Friedel and Crafts' reaction is used. According to Meissel,[7] by the use of this reagent upon a mixture of benzene and carbon tetrachloride, triphenylchlormethane is formed, as by subsequent treatment 75 per cent. of the theoretical amount of triphenylcarbinol can be obtained. "No triphenylmethane is formed in this reaction as is the case when aluminum chloride is employed."

As a matter of fact, however, the action of aluminum chloride upon a mixture of carbon tetrachloride and benzene is exceedingly smooth, provided certain conditions are observed. I have used this reaction many times, and not in a single instance could I detect any trace of triphenylmethane. Friedel and Crafts are entirely correct that triphenylchlormethane is the principal product of the reaction. By observing certain precautions as to temperature of heating and manner of decomposing the chloride of aluminum, the triphenylchlormethane itself can be easily isolated and obtained very pure, with a yield from 70–90 per cent. of the

[1] *Ann. Chem.* (Liebig), **194**, 257.
[2] *Ibid.*, **12**, 1468.
[3] *Ibid.*, **14**, 1523.
[4] *Ibid.*, **28**, 1537; **29**, 1402.
[5] *Ibid.*, **28**, 2792.
[6] *Ibid.*, **30**, 1776; **32**, 2415.
[7] *Ibid.*, **32**, 2422.

theoretical quantity. This forms by far the best method for the preparation of this compound, as by means of it one can easily obtain 500 grams of the pure triphenylchlormethane in less than two days. The chloro compound may, therefore, with advantage replace the triphenylbrommethane in many reactions, as the latter is usually made from the rather expensive triphenylmethane. Even by the method of Allen and Kölliker[1] it cannot always be obtained free from the bromanthracenes.

EXPERIMENTAL PART.

Aluminum Chloride.—Gattermann[2] called attention to the fact that the yield and smoothness of Friedel and Crafts' reaction depend in a great measure upon the purity of the aluminum chloride. He prepared the latter by the action of hydrochloric acid gas upon heated aluminum. This is at present the method generally employed. Biltz[3] has noticed that in some instances pure, freshly prepared aluminum chloride is rather a detriment, and old, slightly deteriorated reagent is to be preferred. That chlorine acts upon metallic aluminum is a fact well known, but has seldom been employed in laboratories for the preparation of the chloride.[4] I find this to be by far the most convenient method of preparing aluminum chloride, especially when one has access to liquid chlorine. The reagent obtained in this manner is very reactive. About 50 grams of aluminum turnings, thoroughly washed and dried, are placed in a combustion tube, the metal being held in place by loose plugs of asbestos wool. The tube is placed in a combustion furnace, one end is connected with the chlorine tank, and the other fits by means of an asbestos stopper into an iron receiver.[5] The portion of the tube nearest to the receiver is now heated, and a *rapid stream* of dry chlorine is passed into the tube. The gas attacks at once the cold portion of the metal, provided the stream of chlorine is quite rapid. The heat of the reaction is very great, and the metal is kept glowing throughout the length of about 3 inches. In about one and one-fourth to one and one-half hours the reac-

[1] *Ann. Chem.* (Liebig), **227**, 110.

[2] Stockhausen u. Gattermann: *Ber. d. chem. Ges.*, **25**, 3521.

[3] *Ibid.*, **26**, 1960.

[4] My attention is called to the fact that Erdmann recommends this reaction in his "Introduction to Organic Preparations," p. 43.

[5] Gattermann: "Praxis des organischen Chemikers," III. Auflage.

tion is finished. The yield is usually 190–200 grams of aluminum chloride, which represents about 80 per cent. of the theory. Sometimes even 90 per cent. can be obtained. By this method 700–800 grams of the chloride can be prepared in one day by using only one furnace. The reagent prepared in this way is very reactive, and retains this property apparently unimpaired even after being kept for two months.

Triphenylchlormethane, $(C_6H_5)_3C.Cl$.—The proportions which were found to give good results are 1 part of carbon tetrachloride, 3.5 parts of benzene, and about 1.25 parts of aluminum chloride. The carbon tetrachloride and benzene were thoroughly dried over calcium chloride and carefully fractionated. The two liquids are placed in a round-bottomed flask connected with a long inverted condenser by an arrangement as suggested by Anschütz.[1] The aluminum chloride is added in portions of about 20 grams each. The reaction becomes very violent. I have not attempted to moderate it by cooling. After all the chloride is added, the mixture is heated on the water-bath for about an hour. The next step, the decomposition of the aluminum chloride, requires certain precautions. The cooled mixture is poured in a slow stream upon a good quantity of pounded ice, the jar containing the latter being itself surrounded with a cooling mixture. The addition of the reaction product to the ice should be done slowly, and with constant stirring. Benzene is also added from time to time in order to keep the triphenylchlormethane in solution. After all has been added the benzene solution is separated from the ice and water by a separating funnel, shaken once with ice-water containing hydrochloric acid, and once with ice-water alone. It is advisable to leave the two solutions in contact with each other as short a time as possible. The filtered benzene solution is dried thoroughly over calcium chloride, and concentrated on the water-bath as far as possible. On cooling, over half of the pure triphenylchlormethane separates in large crystals. These are removed by filtration and washed once or twice with dry ether, in which the chloro compound is not very soluble. The filtrate is distilled first on a water-bath at ordinary pressure, and then concentrated by distilling off the benzene under diminished pressure. To the very concentrated solution dry ether is again

[1] *Ann. Chem.* (Liebig). **235**, 154.

added, and another large portion of the chloro compound is precipitated. This is treated in the same way as the first crop of crystals, and is just as pure, retaining a slight pink color. The mother liquid is subjected once more to the same treatment—evaporating the ether, and concentrating under diminished pressure—and yields a third crop of crystals. By this treatment the triphenylchlormethane is freed from both the coloring-matter and the triphenylcarbinol, since both of these are quite soluble in ether. The last mother-liquid contains all the coloring-matter. In several instances I have evaporated it to a thick sirup, dried on a porous plate, boiled with water, and obtained considerable quantities of triphenylcarbinol,—but never any indication of triphenylmethane. The yield of the pure chloro compound varies from 70–85 per cent. and enough carbinol can be obtained to account for a yield of 90–95 per cent. of the theory.

In the following table are given some of the results obtained:

	Carbon tetrachloride. Grams.	Benzene. Grams.	Aluminum chloride. Grams.	Triphenylchlormethane. Grams.	Per cent. of theory.	Triphenylcarbinol. Grams.
I	300	1000	300	390	72	22
II	360	1500	410	500	71	..
III	39	150	50	51	78	10
IV	129	500	150	201	87	..

It has already been mentioned that the triphenylchlormethane obtained by this reaction is quite pure, and can be employed for most reactions without further purification. It melts usually at 108°–112° C., while Hemilian[1] gives it as 105°–115°. C

The following method was found to give equally good results as Carius' for the estimation of chlorine in this substance. The chloro compound is dissolved in alcoholic potash (2 per cent.) and heated for a short time on the water-bath. The alcohol is evaporated, the residue dissolved in water, filtered from the ethyl ether of triphenylcarbinol, and the chlorine is estimated in the filtrate in the usual manner with silver nitrate.

In the following table are given the results of analysis of I, III, IV of the preceding table. The chloro compound had been obtained in three separate crops. Each crop was analyzed by itself.

[1] *Ber. d. chem. Ges.*, **7**, 1203.

	First crop.	Second crop.	Third crop.	Calculated for $(C_6H_5)_3C.Cl$.
I.....	12.35	12.74	12.69	12.75
III.....	12.45	12.48	12.49	12.75
IV.....	12.62	12.60	12.56	12.75

The product obtained by this method may, therefore, be considered quite pure. For further purification it can be recrystallized from benzene alone, or better by precipitating it from a concentrated solution in benzene by means of dry ether. By this method large quantities of pure triphenylchlormethane can be more easily obtained than by the old method[1],—by treating triphenylcarbinol with phosphorus pentachloride.

In conclusion I wish to express my thanks to Messrs. A. G. Marion, H. W. Emerson, and F. L. Woods for their kind assistance in carrying out some of the experimental work.

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AN INSTANCE OF TRIVALENT CARBON: TRIPHENYLMETHYL.

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[PRELIMINARY PAPER.]

SOME time ago[2] I published a method of preparing tetraphenylmethane. The yield was rather small and I was obliged to study the solubilities, composition, molecular weight, and the nitro derivative on about 0.5 gram of the hydrocarbon. The stereochemical interest attached to this compound has induced me to take up the subject once more, in the hope of obtaining larger yields. I have, therefore, gone over most of the methods which have been tried by others for the preparation of tetraphenylmethane. My results, while differing in detail from those published by others, agree in the main,—the hydrocarbon could not be obtained by the usual reactions. One of the main proofs advanced by me for the constitution of tetraphenylmethane was that it furnished a tetranitro derivative which gave no colored salts with alcoholic potash, while most of the less phenylated methanes do respond to this test. To prove whether

[1] Hemilian: *Ber. d. chem. Ges.*, **7**, 1207.

[2] *Ber. d. chem. Ges.*, **30**, 2043; This Journal, **20**, 773.

this reaction could safely be relied upon I decided to prepare hexaphenylethane, $(C_6H_5)_3C—C(C_6H_5)_3$. This hydrocarbon should by nitration give a hexanitro body with no hydrogen attached to the ethane carbon atoms. Consequently it also should give no colored salts with sodium ethylate or alcoholic potash.

Accordingly, triphenylbrommethane in benzene was treated with metallic sodium, but without success. The chloro compound gave no better results. Molecular silver was substituted for sodium. After several hours' boiling a white crystalline body began to separate, and on filtering the hot benzene solution a considerable amount of the same substance separated on cooling. It was recrystallized from benzene, gave a constant melting-point, 185° C., and contained no halogen. In its high melting-point and in its only slight solubility in the usual organic solvents it resembled closely tetraphenylmethane, and this new body was taken for hexaphenylethane. An elementary analysis gave, however, the following results :

	Calculated for $(C_6H_5)_6C_2$.	Found.
Carbon	93.83	87.93
Hydrogen	6.17	6.04

The low per cent. of carbon found was rather surprising. It was explained on the assumption that this was, perhaps, an instance of a hydrocarbon which is not easily burnt. The next combustion was, therefore, carried on in an atmosphere of oxygen from the very beginning. The substance was mixed in the tube with copper oxide ; a very high heat was applied towards the end of the combustion. The results were as follows :

Carbon	87.74
Hydrogen	6.46

An entirely new lot of the material was then prepared. Ten grams of triphenylchlormethane and 10 grams of silver gave, after several hours' boiling, 4 grams of the same hydrocarbon. This was recrystallized twice from benzene and twice from chloroform. It was perfectly free from halogen, was snow-white, and melted at 185°–186° C. The combustion was again made in an atmosphere of oxygen, lead chromate being used instead of copper oxide.

Carbon	87.77
Hydrogen	6.23

The next analysis was made in a bayonet tube, the tube being filled with fine copper oxide for about four-fifths of its length, to insure combustion of any methane gas which would perhaps otherwise escape. The combustion was carried on slowly, and a very high heat was used towards the end.

Carbon	88.23
Hydrogen	6.34

Several new lots of the same substance were made both from the triphenylbrommethane and triphenylchlormethane, and purified by successive recrystallization from benzene, chloroform, acetic ether, and carbon disulphide. They all gave the same results, entirely concordant with each other. Combustions were then made in a porcelain tube, applying the direct heat of the furnace; also by the moist method with chromic acid in concentrated sulphuric acid,[1] but with no better result. I therefore came to the conclusion that the body under consideration was not a simple hydrocarbon, but an oxygen derivative. The oxygen could come from either of two sources: first, the molecular silver may have contained some oxide of the metal; second, the atmospheric oxygen may act upon the hydrocarbon.

As only the molecular silver, and not the finely powdered crystalline metal appeared to act in this case, a very pure sample of the former was prepared. The moist silver, as obtained by reduction of the chloride with zinc, was digested for a day with dilute sulphuric acid. It was then thoroughly washed by decantation, digested for several hours with ammonium hydroxide, again washed with water, then with alcohol, absolute alcohol, ether, and finally with benzene. This sample of silver gave, however, results not differing from those previously obtained. To make it more certain that the oxygen did not come from the silver, I substituted other metals for it. Mercury and zinc were found to act equally well, if not better, and the yield of the oxygen compound obtained by either of these two metals was even greater than in the case of silver. Another great advantage in the use of zinc and mercury is that the reaction takes place at *ordinary temperature*. Mercury is especially well suited for a

[1] Fritzsche: *Ann. Chem.* (Liebig), **294**, 79.

lecture experiment showing this reaction. If a benzene solution of triphenylchlormethane or triphenylbrommethane be shaken in a test-tube for a few minutes with some metallic mercury and the solution rapidly filtered, the separation of the insoluble oxygen compound in the filtrate will soon begin, due to the absorption of atmospheric oxygen.

I next proved that it is really the oxygen from the atmosphere which oxidizes the hydrocarbon. By working in an atmosphere of carbon dioxide no such insoluble compound is produced, even on weeks' and months' treatment of the halogen bodies with silver, mercury, or zinc in benzene. After a long series of experiments I settled upon zinc as the best reagent with which to carry on this reaction. Ordinary granulated zinc, zinc strips, zinc dust,—all act upon the halogen compounds. In all further experiments what is known as *powdered zinc*, freed from zinc dust by sifting, has been employed. In this form the metal can readily be obtained free from the oxide, is easily handled, has a large surface exposure, and presents no difficulties in filtering from the benzene solution. Triphenylchlormethane[1] has been used altogether instead of the bromine compound.

The successful preparation of the unsaturated hydrocarbon requires the *absolute* exclusion of oxygen from the apparatus. Corks are to be avoided, and even rubber stoppers, exposed to the action of benzene vapors, become after a while porous. I have constructed for this work an apparatus by means of which the reaction can be carried on for several weeks, and months, if necessary. The zinc, benzene, and triphenylchlormethane are first digested for any length of time desired at ordinary temperature; the solution is then filtered into a distilling flask and the zinc washed with fresh portions of benzene. The combined liquids are distilled under diminished pressure at 30° C., and the solid crystalline residue containing the unsaturated hydrocarbon can be examined as to its solubility in different solvents, or treated in any manner desired. The apparatus is so arranged that all these steps are carried on in an atmosphere of dry carbon dioxide. Only ground-glass joints are used. The description of the apparatus is reserved for a future paper.

[1] For the preparation of this see the preceding paper.

I. THE HALOGEN IS TAKEN OUT BY THE ZINC QUANTITATIVELY.

The zinc removes the halogen from triphenylchlormethane quantitatively at ordinary temperature. The zinc chloride separates as a thick dark yellow sirup, probably forming a compound with benzene similar to the one produced by aluminum chloride. This is of very great advantage, because by this means fresh, clean surfaces of the metal are continually exposed for further action. For this reason the reaction is very slow, and soon stops altogether when carbon tetrachloride is substituted for benzene. With 20 grams of triphenylchlormethane, 150 grams of benzene, and 25 grams of zinc the reaction is completed in about five to six days. After removing the benzene solution and washing the residue thoroughly with benzene, the zinc chloride was dissolved in water and the chlorine estimated in the usual way.

	Triphenyl-chlormethane taken. Grams.	Number of days of digestion.	Chlorine as $ZnCl_2$.	Calculated.
I	5	12	12.61	12.75
II	20	5	12.25	12.75
III	20	20	12.41	12.75

II. THE UNSATURATED HYDROCARBON.

The clear filtered solution containing the unsaturated hydrocarbon is concentrated under diminished pressure at a temperature of 30°–35° C., a slow stream of carbon dioxide being used to prevent bumping. When all the benzene has been distilled off, a strong stream of the gas is allowed to bubble through the thick yellow sirup, while the temperature is raised to about 40° C. On cooling, the whole residue solidifies to a crystalline cake, which does not melt even at 60° C. Even after several weeks' standing it redissolves readily in benzene with the exception of some of the oxygen compound whose formation is due to unavoidable leakage of the stop-cocks. The hydrocarbon is quite soluble in chloroform, less so in carbon tetrachloride, and is quite readily dissolved by carbon disulphide. If a concentrated solution of it is allowed to stand for three or four weeks, some large transparent crystals are formed. An attempt was made to remove these and wash with petroleum ether, but before the operation was finished enough oxygen was absorbed to form the

insoluble derivative. I hope to be able to isolate the hydrocarbon itself in a pure state.

The body is extremely unsaturated. A solution of it in benzene or in carbon disulphide absorbs oxygen with great avidity and gives an insoluble oxygen compound. It absorbs chlorine, bromine, and iodine. It does not unite with carbon monoxide.[1]

III. DI-TRIPHENYLMETHYLPEROXIDE,

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3.$$

The crystalline compound which is formed by the action of the atmospheric oxygen upon a solution of the unsaturated hydrocarbon, is the peroxide of triphenylmethyl. It is best prepared by passing air or oxygen through a solution of the hydrocarbon in benzene. Twenty grams of the halogen compound give about 12 grams of the peroxide. The elementary composition fully agrees with that required by the formula:

	Calculated for $(C_6H_5)_6C_2O_2$.	Found. I.	II.	III.	IV.	V.
Carbon.....	88.03	87.93	87.74	87.77	88.22	87.60
Hydrogen.....	5.79	6.04	6.46	6.23	6.34	6.09

This body is characterized by extreme insolubility. It is only with difficulty dissolved by hot benzene, toluene, and then not without some decomposition. It can be recrystallized from chloroform. It is insoluble in ether, alcohol, and water. It is best recrystallized from carbon disulphide, 1 gram dissolving in about 150 cc. of the hot solvent. I have obtained by the use of this solvent remarkably beautiful and regular crystals, six-sided hexagons, of a very high refractive index. The peroxide melts at 185°-186° C. (uncorr.)

It is quite stable on exposure to air but decomposes gradually when a solution of it is heated. For this reason solvents of low boiling-point are to be preferred.

Formation by Means of Sodium Peroxide.—On heating triphenylchlormethane in benzene with commercial barium peroxide for several days a small amount of the triphenylperoxide was obtained. On repeating the experiment with a purified sample of barium peroxide the result could not be duplicated. I have resorted to the use of sodium peroxide, and with this

[1] Compare Nef: *Ann. Chem.* (Liebig), **270**, 267.

reagent I never failed to get the peroxide. A 10 per cent. solution of sodium peroxide is made by dissolving the latter in ice-water. Three to four grams of triphenylchlormethane in just enough benzene to make a clear solution are added, and a stream of air, free from carbon dioxide, is passed through the cold mixture until all the benzene is evaporated. The air keeps the two liquids in constant motion and fresh quantities are continually exposed to action. The solution is now filtered and washed. The unchanged chloro compound and the carbinol are removed by ether and the insoluble residue is boiled up with a large amount of carbon disulphide. The filtered solution gives, on concentration, a small amount of the characteristic crystals of the peroxide. This method was repeated several times, with and without the use of benzene, and has invariably given from 5 to 10 per cent. of the calculated amount of the peroxide. The larger portion of the chloride is changed to the carbinol, as it always does when left in contact with water, especially in presence of alkalies. The peroxide so obtained was identical with the one previously described. An analysis gave the following figures:

	Calculated for $(C_6H_5)_6C_2O_2$.	Found.
Carbon	88.03	87.55
Hydrogen	5.79	6.00

That the formation of the peroxide is really due to the presence of sodium peroxide, and does not result from the oxidation of the chloride or the carbinol by atmospheric oxygen, is shown by the following experiment: Three grams of the chloride dissolved in 10 cc. of benzene, were added to 100 cc. of a 10 per cent. solution of sodium hydroxide, and air was passed through the flask exactly in the same way as when sodium peroxide was used. On working up the product not a trace of triphenylmethyl-peroxide was found.

Molecular Weight.—Attempts to get an exact determination of the molecular weight have not proved as successful as desired. The peroxide is only slightly soluble in the usual organic solvents, and, therefore, only a slight elevation of the boiling-point could be expected, from 0.003°-0.150° C. I have found no liquid or low-melting solvent which could be used for the freezing-point

method. In using the boiling-point method it was found necessary to select as low-boiling a solvent as possible, since the peroxide suffers gradual decomposition at higher temperatures. Carbon disulphide was tried first. As the solubility of the peroxide in this solvent is only about 1 gram in 150 cc., the maximum rise of temperature could not be expected to be above 0.040° C. I therefore constructed an apparatus similar to the one described by Jones.[1] From 100–200 grams of the solvent could then be employed for a single determination. By this means the influence of the absolute error due to the weighings, vaporization of the solvent, etc., is greatly reduced. The apparatus proved very reliable, and the solvents employed could be kept boiling for an hour with a variation of temperature not exceeding 0.002° C. Tested on triphenylmethane the apparatus gave a molecular weight of 252 (244 calculated) when 1.2862 grams of the substance and 113 grams of the solvent were employed. The rise of temperature was to 0.107° C.

SOLVENT : CARBON DISULPHIDE. K = 2370.

Carbon disulphide. Grams.	Peroxide. Gram.	Rise in boiling-point.	Calculated rise for $m = 518$.	Molecular weight.
121.7	0.7300	0.035	0.028	406

The temperature remained constant for about fifteen to twenty minutes; after that it gradually began to rise, about 0.001 every ten minutes. The experiment was interrupted when 0.045 was reached. The solution was yellowish, showing slight decomposition of the peroxide.

SOLVENT : BENZENE. K = 2770.

Benzene. Grams.	Peroxide. Grams.	Rise in boiling-point.	Calculated rise for $m = 518$.	Molecular weight.
66	0.853	0.09	0.070	448

This temperature remained constant for about ten minutes, after that the rise was gradual until in an hour it reached 0.185° C. The solution was then quite yellow.

Ethylene dibromide was also tried, but as this boils still higher, there was even more rapid decomposition. The results in the main agree with those obtained when benzene was used.

The only conclusion that can be safely drawn from these results is that we have here a substance of very high molecular

[1] *Am. Chem. J.*, **19**, 581.

weight, above 400 at least. The formula for the peroxide would require 518.

Conversion of the Peroxide into the Carbinol.—The peroxide dissolves in cold concentrated sulphuric acid with considerable evolution of heat, giving a yellow solution which soon turns dark, and finally almost black. The sulphuric acid does not induce any explosion as is the case with most organic peroxides. On diluting the acid with water the triphenylcarbinol is precipitated out as a dark flocculent precipitate.

2.85 grams of the pure peroxide were dissolved in 25 cc. of sulphuric acid and allowed to stand over night. The solution was then poured upon ice and the precipitate separated by filtration. It was dissolved in ether, and the dark ethereal solution was repeatedly shaken with dilute sodium hydroxide until the ether was only of a pale yellow color. The dried ethereal solution was then concentrated to a small bulk and rhigolene added. Crystals of triphenylcarbinol separated and were almost pure, melting at 159°–160° C. The yield was 1.948 grams, which represents 70 per cent. of the peroxide taken. The mother-liquid, on concentration, gave additional 0.215 gram, and 0.050 gram was obtained from the third crop, making a total of almost 80 per cent. The remaining 20 per cent. were probably oxidized by the oxygen evolved or perhaps sulphonated, as the sodium hydroxide removes all the dark color from the ethereal solution. An analysis gave the following results:

0.2910 gram substance gave 0.9330 gram carbon dioxide and 0.1654 gram water.

	Calculated for $(C_6H_5)_3C.OH$.	Found.
Carbon	87.69	87.44
Hydrogen	6.15	6.31

The reaction may therefore be represented by the following equation:

$$\begin{matrix}(C_6H_5)_3C{-}O\\ \quad\quad|\\ (C_6H_5)_3C{-}O\end{matrix} + H_2O = \begin{matrix}(C_6H_5)_3C.OH\\ \\ (C_6H_5)_3C.OH\end{matrix} + O.$$

Di-trinitrotriphenylmethylperoxide, $(C_6H_4NO_2)_3C-O-O-C(C_6H_4NO_2)_3$.—Brodie,[1] Vanino,[2] and Nef[3] have shown that the

[1] *Ann. Chem.* (Liebig), Suppl. III, 209.
[2] *Ber. d. chem. Ges.*, **30**, 2004; **33**, 1045.
[3] *Ann. Chem.* (Liebig), **298**, 287.

superoxides of acid radicals can be nitrated with fuming nitric acid. The peroxide here described shares the same property. It forms very readily a hexanitro compound. One gram of the peroxide gave 1.375 grams of the pure nitro body, while theory requires 1.555 grams. The nitro compound is insoluble in the usual organic solvents. One gram refuses to dissolve completely in 500 cc. of boiling glacial acetic acid. It is best recrystallized by dissolving it in nitrobenzene at 120°–130° C., and precipitating with petroleum ether.

	Calculated for $C_{38}H_{24}N_6O_{14}$.	Found. I.	II.
Carbon	57.87	57.55	....
Hydrogen	3.05	3.34	....
Nitrogen	10.65	11.03	10.94

IV. TRIPHENYLIODOMETHANE, $(C_6H_5)_3C.I.$

The unsaturated hydrocarbon, which is formed when the halogen is removed from triphenylchlormethane, unites not only with oxygen, but also instantly with chlorine, bromine, and iodine. The reaction with chlorine and bromine is, however, not one of mere addition. The hydrocarbon is so reactive that even at —10° C. chlorine and bromine act both by addition and substitution. When the hydrocarbon, entirely freed from benzene, is dissolved in carbon tetrachloride there is always some hydrochloric and hydrobromic acid produced on the addition of the halogen. Triphenylchlormethane and triphenylbrommethane are among the products but it is not easy to separate the substitution halogen-compounds formed at the same time. This reaction will be further studied.

Iodine is absorbed by the hydrocarbon as readily as the other two halogens. When a solution of the hydrocarbon in carbon disulphide is treated at 0° C. with a solution of iodine in the same solvent, the latter is instantly decolorized. The end-reaction is quite sharp. In one instance, working with a product from 20 grams of triphenylchlormethane, 6 grams of iodine were absorbed, which is equivalent to 12 grams of $(C_6H_5)_3C—$; in another case, where 25 grams of the chloro compound were employed, the absorption amounted to 8 grams of iodine. The isolation of the iodo compound requires considerable precautions, as it is a very

unstable body. I have found it best to work in an atmosphere of dry carbon dioxide, but am not as yet prepared to say whether it is the oxygen or the moisture of the air that affects it most. Probably it is the latter. The solution of the iodo compound was filtered to remove a slight amount of a periodide[1] and the peroxide. To the clear carbon disulphide solution rhigolene was added and the mixture cooled in ice. After some crystals had separated the liquid was transferred to another flask and cooled again, when more crystallized out. This last crop was recrystallized by dissolving it in carbon disulphide and precipitating with rhigolene. The crystals were of a pale yellow color, the same in appearance as the chloro compound when the latter is similarly precipitated. The crystals were washed several times with rhigolene and dried rapidly *in vacuo*.

The iodine was estimated by treating a weighed sample of the compound in dilute alcohol with ammonia and zinc dust. The hot alcoholic solution was filtered, the zinc washed thoroughly with hot alcohol, and then with water. The alcohol washings were concentrated, filtered, and the residue was exhausted with water. The insoluble portion was purified with ether, and was identified as triphenylcarbinol. It melted at 153° C., probably due to the presence of some triphenylmethane. On recrystallizing twice from alcohol the melting-point was raised to 157°–159° C. The yield of the carbinol was 0.383 gram, while the calculated quantity for the 0.602 gram of triphenyliodomethane was 0.422 gram.

0.602 gram substance gave 0.3704 gram AgI.

	Calculated for $(C_6H_5)_3C.I.$	Found.
Iodine	34.29	33.23

The iodide turns dark very readily and loses iodine. It is very unstable. It melts approximately at 135° C., with decomposition. Water, especially in the presence of alkalies, converts it into triphenylcarbinol, a reaction similar to that with the corresponding chloro and bromo compounds. Alcohol, however, behaves in this case differently. On boiling with alcohol large quantities of iodine are set free and the body is reduced by the

[1] For a periodide of triphenylbrommethane, see this Journal, **20**, 790.

alcohol to triphenylmethane, while in the case of triphenylchlormethane and triphenylbrommethane the ethyl ether,

$$(C_6H_5)_3C.OC_2H_5,$$[1]

is formed. The triphenylmethane was freed from a small amount of the unreduced ether by fractional crystallization from alcohol, and was identified by its characteristic crystals containing benzene of crystallization and melting at 77° C. On exposure to air the benzene of crystallization was lost and the crystals melted at 92° C.

V. TRIPHENYLMETHYL, $(C_6H_5)_3\equiv C.$

The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, $(C_6H_5)_3\equiv C$. On this assumption alone do the results described above become intelligible and receive an adequate explanation. The action of zinc results, as it seems to me, in the mere abstraction of the halogen, leaving the free radical,

$$(C_6H_5)_3C.Cl + zn = (C_6H_5)_3C + znCl.$$

The radical so formed is apparently stable, for it can be kept both in solution and in the dry crystalline state for weeks. The radical refuses to unite with another one of its kind, and thus forms a distinct exception to all similar reactions. It might be said that, perhaps, it does polymerize to hexaphenylethane, $(C_6H_5)_3C—C(C_6H_5)_3$, but this hydrocarbon is so unstable that mere exposure to air is sufficient to break it down. Such an assumption seems to me less tenable than that of a free radical. Hexaphenylethane must, according to all our present notions of valence, be a saturated compound. Yet the hydrocarbon under consideration is decidedly unsaturated. We know of no better positive test for unsaturation in hydrocarbons than the absorption of halogens. Perhaps chlorine and bromine would in this case attack and decompose hexaphenylethane, if that be the hydrocarbon; but, certainly, a dilute solution of iodine, at 0° C., would scarcely do that. It seems to me rather that hexaphenylethane, once formed, would prove quite a stable compound. This may be justly inferred from analogous reactions, where a

[1] Hemilian: *Ber. d. chem. Ges.*, 7, 1208.

fourth heavy radical has been successfully introduced into the methane,—as is the case with triphenylthiophylmethane, $(C_6H_5)_3.C.C_4H_4S$,[1] tetraphenylmethane, $(C_6H_5)_3C.C_6H_5$,[2] triphenylacetic acid,[3] etc. It is a phenomenon parallel to that expressed by V. Meyer's esterification law of diortho substituted aromatic acids: It is very difficult to introduce an alkyl into the carboxyl of such acids by the *usual method* of esterification, but once introduced, it is just as difficult to remove it again.

On the assumption of the existence of triphenylmethyl itself, as such, all the reactions of the unsaturated body become clear. Oxygen adds itself, a whole molecule, and gives the peroxide:

$$\begin{matrix}(C_6H_5)_3{\equiv}C \\ (C_6H_5)_3{\equiv}C\end{matrix} + \begin{matrix}O \\ \| \\ O\end{matrix} = \begin{matrix}(C_6H_5)_3{\equiv}C{-}O \\ | \\ (C_6H_5)_3{\equiv}C{-}O\end{matrix}.$$

The addition of a molecule of oxygen is entirely in accord with the recent studies of M. Traube, van 't Hoff, Engler, Manchot, Bach, Baeyer and Villiger, and Nef. This case forms an excellent illustration of Engler's[4] theory that "autoxidation" results first of all in the formation of superoxides. The action of halogens upon the unsaturated body is primarily that of addition. Thus iodine gives triphenyliodomethane:

$$\begin{matrix}(C_6H_5)_3{\equiv}C \\ (C_6H_5)_3{\equiv}C\end{matrix} + \begin{matrix}I \\ | \\ I\end{matrix} = \begin{matrix}(C_6H_5)_3{\equiv}C{-}I \\ \\ (C_6H_5)_3{\equiv}C{-}I\end{matrix}.$$

That the unsaturated hydrocarbon is not the result of some complicated reaction between triphenylchlormethane, benzene, and the nascent zinc chloride formed during the experiment, is proved by the following: 5 grams of the halogen compound were dissolved in 100 cc. of carbon disulphide and shaken at intervals with 100 grams of metallic mercury for two days. The clear filtered solution on exposure to air furnished 3.8 grams of triphenylmethyl peroxide. Five grams of triphenylchlormethane, treated with zinc and benzene for four days, gave 3.1 grams of the peroxide.

The existence of triphenylmethyl implies, of course, the existence of *trivalent carbon*, at least in this particular instance. The

[1] Weisse: *Ber. d. chem. Ges.*, **28**, 1538.

[2] Gomberg: *Ibid.*, **30**, 2043.

[3] E. and O. Fischer: *Ann. Chem.* (Liebig), **194**, 260; Heyl and V. Meyer: *Ber. d. chem. Ges.*, **28**, 2782.

[4] *Ber. d. chem. Ges.*, **30**, 1669; **33**, 1090, 1097.

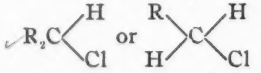
conception of such a trivalent carbon in this instance is entirely distinct from that which is ascribed to it by some in benzene, or even in ethylene, where there are always *two* adjoining carbon atoms acting as trivalent. The unsaturation in such cases has always been indicated by a "double linking." In triphenylmethyl there is *only one carbon atom* that is unsaturated. The existence of such a body means that when three valences of carbon are taken up by three phenyl groups it is difficult, or perhaps even impossible, to introduce as a fourth group such a complicated radical as $(C_6H_5)_3C$—. Only simpler groups, chlorine, bromine, iodine, oxygen, etc., may still combine with such a carbon atom. Whether this be due to the negative character of the three phenyl groups, or whether it is caused by the fact that these groups take up so much space around the carbon atom as to hinder the introduction of another complicated group, is a question of an entirely different nature and need not be discussed here. There are, however, numerous reactions which go to show that there is a limit to the number of complicated groups which can ordinarily be linked to one and the same carbon atom. A few of these reactions may be mentioned.

Hemilian,[1] Friedel and Crafts,[2] E. and O. Fischer,[3] Magati,[4] Schwartz,[5] V. Meyer,[6] Weisse,[7] Waga,[8] and Meisel,[9] have all attempted to prepare tetraphenylmethane, but in all cases triphenylmethane resulted. Even such comparatively simple compounds as $(C_6H_5)_3C.C_2H_5$,[10] or $(C_6H_5)_3C.CH_3$,[11] could not be obtained by reactions from which, *a priori*, we should certainly expect the formation of such bodies. The disinclination of carbon to hold more than three complicated groups is well illustrated by the results of Anschütz's[12] extended researches on tetraphenylethane. A large number of methods which ought to give the unsymmetrical derivative, $(C_6H_5)_3C.CH_2(C_6H_5)$, always

[1] *Ber. d. chem. Ges.*, **7**, 1209.
[2] *Ann. chim. phys.*, 1884, I, 497.
[3] *Ann. Chem.* (Liebig), **194**, 254.
[4] *Ber. d. chem. Ges.*, **12**, 1468.
[5] *Ibid.*, **14**, 1523.
[6] *Ibid.*, **28**, 2792.
[7] *Ibid.*, **28**, 1538; **29**, 1402.
[8] *Ann. Chem.* (Liebig), **282**, 330.
[9] *Ber. d. chem. Ges.*, **32**, 2422.
[10] E. and O. Fischer: *Ann. Chem.* (Liebig), **194**, 259.
[11] Biltz: *Ibid.*, **296**, 253.
[12] *Ibid.*, **235**, 203.

give the symmetrical one, $(C_6H_5)_2CH.CH(C_6H_5)_2$. And lastly, the abnormal behavior of tetraphenylethylene towards bromine, as found by Biltz,[1] shows again the same point. Bromine will substitute in, but not add itself to, tetraphenylethylene, although we have here an unsaturated linking, $(C_6H_5)_2C : C(C_6H_5)_2$. These and a number of other facts show conclusively that with three valences of carbon taken up by such complicated or large groups as phenyl, the fourth valence can ordinarily be linked to atoms or groups of simple construction only. Now, as a result of the removal of halogen from triphenylchlormethane in benzene by zinc, or in carbon disulphide by mercury, the fourth valence of the methane carbon is bound either to take up the complicated group $(C_6H_5)_3C—$, and polymerize, or remain as such, with carbon as trivalent. Apparently the latter is what happens.

In conclusion, it may be mentioned that the action of metals upon triphenylhalogenmethane has been tried before. Elbs[2] acted upon triphenylbrommethane with sodium, magnesium, and copper. Anschütz[3] employed sodium upon a mixture of triphenylbrommethane and benzyl chloride. The action of metals upon the di- and monophenylhalogen methanes has also been extensively studied. While diphenyldichlormethane loses all its halogen and gives tetraphenylethylene, compounds of the type



lose halogen acid. Thus, benzyl chloride, when treated with zinc,[4] zinc-copper couple,[5] gives polymers and reduction-products of phenylmethylene. Recently Nef[6] has used aluminum chloride upon benzyl bromide in the hope of splitting off hydrobromic acid and thus obtaining the free radical phenylmethylene, $(C_6H_5)CH$. The formation of the latter as an intermediate product was made quite probable, but the isolation of it proved impossible, owing to a rapid polymerization.

This work will be continued and I wish to reserve the field for myself.

UNIVERSITY OF MICHIGAN,
CHEMICAL LABORATORY,
August, 1900.

[1] Ann. Chem. (Liebig), **296**, 231.
[2] *Ber. d. chem. Ges.*, **17**, 700.
[3] *Ann. Chem.* (Liebig), **235**, 226.
[4] Zinke: *Ibid.*, **159**, 1368.
[5] Gladstone and Tribe: *J. Chem. Soc.*, **45**, 154; **47**, 448.
[6] *Ann. Chem.* (Liebig), **298**, 248.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 52.]

THE SEPARATION OF TUNGSTEN TRIOXIDE FROM MOLYBDENUM TRIOXIDE.

BY MAX J. RUEGENBERG AND EDGAR F. SMITH.

Received September 7, 1900.

THE separation of tungsten from molybdenum is always of interest to those who are brought in contact with analytical methods. It has been the subject of numerous investigations and much discussion, and while comparatively good methods exist for this purpose, the analyst continues to seek for others, hoping that eventually he shall find a procedure which will be satisfactory in all respects and under nearly all conditions.

The writers have not discovered the method *par excellence*, but desire to offer briefly, in the following lines, their experience in pursuing a suggestion made in an article emanating from this laboratory; *viz.*, "tungstic acid is .... insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this deportment a very simple and exact method for the separation of the two metals."[1]

No analytical data accompanied this declaration; therefore it seemed not improper to attempt to learn the conditions most favorable for the separation. Upon trial it was found that sulphuric acid of specific gravity 1.378, dissolved molybdenum trioxide very readily and apparently did not affect the tungsten trioxide. Acid of this concentration was, therefore, used with the following mixture of the two oxides:

I. 0.7355 gram of tungsten trioxide and 0.0185 gram of molybdenum trioxide were digested for a few minutes with 25 cc. of warm sulphuric acid. The insoluble portion was filtered out and washed with water containing sulphuric acid. After drying it was ignited and weighed. It equaled 0.7350 gram.

The other trials, conducted in precisely the same manner, were as follows:

	II. Grams.	III. Grams.	IV. Grams.	V. Grams.	VI. Grams.
Tungsten trioxide taken	1.0638	0.0871	0.3588	0.8868	0.5996
Molybdenum trioxide taken	2.2712	0.6871	1.1836	1.1986	1.0770
Tungsten trioxide found ...	1.0630	0.0870	0.3587	0.8866	0.5996

[1] EN. D. DESI: This Journal, 19, 242.

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together this mode of separation is apparently of value and merits consideration.

A weighed quantity of a ferric salt equivalent to 5 grams of ferric hydroxide was precipitated with ammonia water and the resulting precipitate, after being washed, was mixed in a beaker with different amounts of tungsten trioxide, and the resulting mixture was then digested with sulphuric acid of the strength of that used in the preceding experiments. The residual oxide was treated as before :

	I. Grams.	II. Grams.	III. Grams.	IV. Grams.	V. Grams.	VI. Grams.
Tungsten trioxide taken ..	0.5282	0.2087	1.3270	0.2004	0.9091	0.2263
Ferric hydroxide taken ...	5.0000	5.0000	5.0000	5.0000	5.0000	5.0000
Tungsten trioxide found ..	0.5278	0.2086	1.3265	0.2003	0.9088	0.2262

We may conclude from these trials that the solubility of the trioxide in the sulphuric acid is in no wise affected by the presence of the iron.

UNIVERSITY OF PENNSYLVANIA.

NEW BOOKS.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY, AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES, TO THE END OF 1899. EDITED BY RICHARD P. ROTHWELL. Vol. VIII. Large 8vo. xxviii+986 pp. With many illustrations. New York: The Scientific Publishing Co. Price, $5.00.

This new annual volume of a well-known and greatly valued series fully sustains the reputation already obtained. The difficulty in obtaining accurate information of this character is well known, and the rapid publication of a large volume like this, requiring the cooperation of so many persons, reflects the greatest credit upon all those concerned in it. The year 1899 was a great year for the mineral industry in the United States, the production in nearly all metals and minerals showing a decided increase. This is especially noticeable in Portland cement, where the increase is from 3,584,586 barrels of 400 lbs. in 1898 to 5,805,620 barrels in 1899. Among the new products listed in recent years are ferromolybdenum, 6,000 lbs. in 1899; molybde-

num, 30,000 lbs.; tungsten, 45,000 lbs.; and Fuller's earth, 13,360 tons.

Among special articles of note are those on "Progress in the Aluminum Industry," by John B. C. Kershaw; "The Occurrence and Genesis of Californian Asphalt," by A. S. Cooper; "Notes on the Metallurgy of Bismuth," by W. Borchers; "Calcium Carbide," by John B. C. Kershaw; "The Hydraulic Cement Industry in the United States in 1899," by Frederick H. Lewis; "Notes on the Metallurgy of Chromium," by W. Borchers; "Notes on the Coarse Pottery Production of Great Britain," by Wilton P. Rix; "Fuel and Its Economical Utilization," by William Kent; "Progress in the Electrolytic Refining of Copper during 1899," by Titus Ulke; "Hofmann's Method for the Manufacture of Blue Vitriol," by Ottokar Hoffmann; "The Cutting and Polishing of Precious Stones," by Leopold Claremont; "Glass," by Robert Linton; "Rare Elements," by Victor Lenher; "The Electrolytic Production of Caustic Soda," by Alfred T. Weightman; "The Manufacture of Sulphuric Acid Stronger Than Chamber Acid," by F. J. Falding; and "The Sulphur Industry of Italy," by Giovanni Aichino.

This list is only a partial one. Many of the articles are illustrated, and not a few contain real contributions to the literature of the subjects treated. E. H.

ANNALI DEL LABORATORIO CHIMICO CENTRALE DELLE GABELLE. DIRETTI DEL DR. VITTORIO VILLAVECCHIA. VOL. IV. Roma Tipografia Elzeviriana, di Adelaide ved. Pateras. 1900. 528 pp.

The report of the Central Chemical Laboratory of the Italian Customs, Vol. IV, by Dr. Vittorio Villavecchia for the years 1898 and 1899 contains nineteen papers or reports on the methods of analysis or examinations of the character of manufactured articles and natural products which are of commercial importance to the country. They comprise the following.

1. "The Composition of Wines Imported into Italy during the Period from 1890–1897." V. Villavecchia.

2. "Methods for the Analysis of the Essential Oils of Bitter Fruits (Lemon, Orange, Bergamot)." G. Fabris. Contains interesting details of the methods of extraction as well as an account of the composition of the pure essences and the methods of detecting adulteration. The principal adulterant seems to be

oil of turpentine but the detection of its presence in small proportion does not seem very certain.

3. "Artificial Turpentine." G. Fabris.

4. "On the Analysis of Coal Tar and Its Preparations." G. Fabris.

5. "Contribution to the Analysis of Oils." M. Tortelli and R. Ruggieri.

I. The detection of cottonseed oil, oil of sesame, and peanut oil in olive oil.

II. The quantitative determination of peanut oil.

6. "A Method for Determining the Absolute Iodine Index of Fatty Substances." M. Tortelli and R. Ruggieri.

7. "The Oil and Wax (Vegetable Tallow) of the *Stellingia Sebifera*." M. Tortelli and R. Ruggieri.

8. "The Composition and Analysis of Vermouth." A. Bianchi.

9. "A Modification of Milliau's Test for the Presence of Cottonseed Oil." G. Armani.

10. "Boiled Vegetable Oils and Their Detection in Admixture with Other Oils." Tortelli and Ruggieri.

11. "The Quantitative Determination of Invert Sugar and Glucose in the Presence of Dextrine." A. Bianchi.

12. "The Determination of the Point of Solidification of Fatty Acids." R. Morischini.

13. "The Analysis and Composition of Certain Qualities of Commercial Bread." G. Fabris and D. Marino.

14. "On the Heating of Certain Gums Used in the Manufacture of Varnishes." G. Armani.

15. "The Characteristics and the Illuminating Power of Stearine, Parraffin, and Spermaceti Candles." R. Ruggieri.

16. "A Contribution to the Knowledge of the Distinctive Characteristics and the Illuminating Power of American Petroleum as Compared with the Russian." G. Rossi.

17. "The Chemical Analysis of Commercial Inks." G. Malagnini.

18. "A Study of the So-called Spices or Powdered Condiments of Commerce." S. Camilla.

19. "Artificial Silks and the Tests to Distinguish Them from Natural Silks." A. Salaro.

Most of these papers are interesting and valuable but from their nature they are difficult to abstract.

The number of samples examined in the laboratory in 1898 was 6,158; in 1897, 5,533. The majority of these consisted of beer, wine, and oils, but almost everything dutiable is represented.

ANDREW A. BLAIR.

(1) EXPERIMENTAL CHEMISTRY. By L. C. NEWELL. 12 mo. xvi+410 pp. 114 illustrations. D. C. Heath & Co. Price, $1.10.

(2) THE ELEMENTS OF INORGANIC CHEMISTRY. By W. A. SHENSTONE. London: Edward Arnold. 12mo. xii + 506 pp. 142 illustrations.

(1) The purpose of this book, as the preface states, "is to promote the more efficient teaching of chemistry by modern methods. The choice and arrangement of subject-matter is based on the author's extended experience with students of varied ability. The book as a whole is the outcome of a desire to provide a course in chemistry which shall be a judicious combination of the inductive and deductive methods." Considerable care has been taken to eliminate errors since it appears from the preface that the entire MS. has been read by three other teachers of chemistry and the proof by fourteen.

Laboratory methods are given prominence—there are 201 experiments in all—and the interrogation point is freely used; some teachers will think too freely. Sixteen pages are included in the chapter on acids, bases, and salts and 25 under atoms, molecules, and related subjects. This latter chapter is open to serious criticism. The statements contained in it are well enough, but such topics as the methods for determining atomic weights, ions and ionization and applications of the theory of electrolytic dissociation, are out of place in a first book on chemistry. When teachers of chemistry learn not to give as a first course more than is necessary, and to follow this up by supplementary courses, we shall have better results. Shooting over the heads of students is still the most common fault in text-books and teachers. The book is an excellent piece of work mechanically.

(2) Like the book noticed above this is evidently intended as a first book in chemistry. The author says: "I have endeavored to provide a book which begins with a course of experimental work for quite young students and develops at the later stages

into a text-book suitable for those who are older; that is, into a text-book containing fewer facts than those written solely for senior students." Part I contains a concise and well-written introduction treated under the captions: "The Chemistry of Fire; Gain of Weight and Combustion; Lavoisier's Researches on Combustion; Is Matter Indestructible? Can We Create It? and Principle of the Conservation of Mass." These topics are briefly treated and in language easily comprehended by a beginner and are illustrated by experiments to be performed by the student.

Chapters II and III contain an introductory study of water, illustrated by experiments which teach methods of determining melting- and boiling-points, the use of the barometer, fractional and destructive distillation, the pipette, specific gravity determinations, etc. Chapter IV tells how to dissolve, crystallize, the use of plotted curves to show solubility, the desiccator, etc. Chapter V treats of the electrolytic decomposition of water, the chemical elements, compounds and mixtures, synthesis, analysis, substitution, and double decomposition. Chapter VI continues the study of water and treats of water of crystallization, the nature of solution, the action of water with the metals, the composition of water by weight, the law of constant proportions, hydrogen peroxide, and the law of multiple proportions.

Chapter VII is a study of the atmosphere, combustion, flame, plants, and animals.

Part I as outlined above covers 94 pages and contains not a single symbol. In Part II chemical nomenclature is taken up and the rest of the book follows, in great measure, the ordinary line of treatment. Here again too much is given, but in other respects the book is a good piece of work and worth the careful study of teachers. E. H.

AIR, WATER AND FOOD FROM A SANITARY STANDPOINT. BY ELLEN H. RICHARDS AND ALPHEUS G. WOODMAN. First edition. First thousand. New York: John Wiley & Sons. 1900. 226 pp. Price, $2.00.

This is an extremely practical book dealing with the common problems of sanitary science in a simple yet thorough manner, and one can not read it through without being convinced that the authors know from their own observations what they are

writing about. After a brief general introduction we find 33 pages devoted to the study of the atmosphere, its general composition, usual contaminations, methods of ventilation, and methods of air analysis from the sanitary standpoint. Then follow, in 78 pages, 3 chapters on water in which many subjects besides those of analysis are discussed. Chapter V is supposed to be written from the "Householder's Standpoint," and Chapter VI from that of the chemist, but both may be read with interest and profit by persons who are not chemists and who have had no training in chemistry beyond that given in ordinary college courses. It is pleasing to see that the authors are not over-impressed with the importance of bacterial analysis in the practical investigations of water. Chapter VII contains a good collection of analytical methods and from the well-known experience of the authors in these matters it will prove valuable to those employed either as teachers of sanitary chemistry or as practical analysts.

The following 75 pages of the book deal with questions of food and partly from the popular standpoint. Many pertinent suggestions are made on the adulteration of common articles, and in the last chapters analytical methods are given by which the practical purity or value of a number of products may be determined. The book closes with a collection of tables, directions for making standard reagents, and with a bibliography of important books and papers dealing especially with topics discussed in the previous pages. J. H. LONG.

ESSENTIALS OF MEDICAL AND CLINICAL CHEMISTRY WITH LABORATORY EXERCISES. BY SAMUEL E. WOODY, A.M., M.D. Fourth edition. Revised and enlarged. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1900. viii+235 pp.

In this book, as in many others of its class, we find an attempt to present what the author considers as the "essentials" of medical chemistry, so-called, within the limits of a single small volume. The space devoted to general and inorganic chemistry, with experiments and qualitative tests, amounts to 124 pages; organic chemistry takes up 47 pages, and clinical chemistry, covering urine analysis and the examination of milk, saliva, and gastric juice, 50 pages more. A very good index completes the book. The author has condensed a good deal of information

(not all of it quite accurate) within the rather narrow limits of the volume and it must be admitted that if the medical student should actually learn all that is there presented he would know much more than the average student carries away with him. But it seems to the present writer that the best selection of matter has not always been made, and that in his effort to be brief the author has very often sacrificed accuracy and clearness. Thus, we find as the definition of an alcohol the following, p. 144: "An alcohol is generally regarded as the hydrate of a hydrocarbon radical, since its formula always has a hydrocarbon radical at its positive end, and the radical HO at the negative end."

It is true that medical students can not devote a large portion of their time to the study of chemistry, but in the time they do spend in elementary chemistry their instruction should be as accurate and systematic as that given to students in the freshman or sophomore years of general colleges. It is a mistake to suppose that there is one kind of elementary chemistry for the clergyman, another for the lawyer, and a third (and the briefest of all) for the doctor. It is the present writer's opinion that the book before him does *not* contain the essentials which a medical man should know. J. H. LONG.

AN OUTLINE OF THE THEORY OF THERMODYNAMICS. By EDGAR BUCKINGHAM, Associate Professor of Physics and Physical Chemistry in Bryn Mawr College, Bryn Mawr, Pa. xi + 205 pp. New York: The Macmillan Company, 1900. Cloth. Price, $1.90.

This book is intended to bridge over the gap that exists between the ordinary text-books on thermodynamics and the modern memoirs on the subject. As the title indicates, special stress is laid on the theory, applications being introduced solely for the purpose of illustration. The subject is treated in 13 chapters, the topics considered being: Thermometry, Calorimetry, Material Systems in Thermodynamics, First Law, Principles of Thermochemistry, Calorimetric Properties of Fluids, Second Law, General Equations, Conditions of Thermodynamic Equilibrium, Thermodynamic Potentials, and Free Energy. One chapter is devoted to recapitulation and two to applications, while an appendix contains a list of useful books. The book is also provided with an index.

In treating his subject, the author begins with the explanation of simple fundamental concepts and gradually leads on to the more difficult relations involved; so that the book (though intended to bridge over a gap, as above stated) is yet complete in itself. The presentation is clear; and the student of thermodynamics will find the book a real aid in mastering the subject. The growing importance of thermodynamics in chemistry will insure for this volume a welcome on the part of chemists.

The work of the publishers is excellent.

LOUIS KAHLENBERG.

THE OIL CHEMISTS' HANDBOOK. By ERASTUS HOPKINS, Chemist in charge of the U. S. Laboratories at Boston, Mass. New York: John Wiley & Sons. 8vo. Price, $3.00.

This book gives, in a clear and concise form, the principal methods of testing the animal and vegetable fats, waxes, and oils, the mineral oils being considered only so far as they occur as adulterants.

A peculiar feature of the work is the tables of the properties and analytical constants of the oils; these have been selected with the greatest care from the original sources, the maximum, minimum, and mean values being given. Their arrangement is numerical; *i. e.*, in the table of the iodine value, the oil having the highest comes first, so with the other constants. These are especially valuable and convenient, as information is obtained at a glance which would take some time to find were it in the body of the book. It is, however, not exclusively a compilation but includes the results of years of practical experience. It seems to the reviewer that in some cases the original method has been adhered to, to the exclusion of the experience of others in the subject. For example the method of Livache is given, as detailed by him in 1886, without stating the experience of Weger and Lippert in 1898 and 1899. So too with regard to the Bechi test, the early procedure employing colza oil (which has since been shown to be unnecessary) is described without giving all the precautions shown to be needful to obtain reliable results; no results of later work are given. Regarding the determination of viscosity it would seem that the statement should have been made that for technical work the Saybolt,

Redwood, or Engler viscosimeter should be employed, rather than a pipette which is no longer much used.

In the matter of references the volume leaves something to be desired, many of the later being omitted, especially in connection with the iodine value. No mention could be found of the heat of bromination test for oils although the valueless sulphur chloride test is given; nor of Halphen's test for cotton-seed oil, one of the most reliable.

There are, too, certain errors of proof-reading and statement which are not in accord with the usual ideas; for example the use of 5.0 instead of 50.0 grams of oil (p 22) for the Maumené test; and in the tables the specific temperature reaction of Gill and Hatch does not refer to the Maumené test but to the heat of bromination test as will be seen from their article.[1] On p. 52. "All good cylinder oils are a mixture of fatty acids and mineral oils;" the cylinder oil should not contain free fatty acids, as most railroad specifications require "acidless animal oil." "Most blown oils are a mixture of fatty acid and mineral oils," being all that is stated about "blown oils," implies that mineral oil is a normal constituent instead of an occasional adulterant.

The tables, however, make the book very valuable and it will doubtless be found very useful to the trade and profession.

AUGUSTUS H. GILL.

BOOKS RECEIVED.

The Oil-Chemists' Handbook. By Erastus Hopkins, A.M., B.Sc. New York: John Wiley & Sons. 1900. viii + 72 pp. Price, $3.00.

The Elements of Inorganic Chemistry, for Use in Schools and Colleges. By W. A. Shenstone, F.R.S. London: Edward Arnold. 1900. xii + 506 pp. Price, 4s., 6d.

Experimental Chemistry. By Lyman C. Newell, Ph.D. Boston: D. C. Heath & Co. 1900. xv + 410 pp.

Fruit Diseases and How to Treat Them. Bulletin No. 66. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 38 pp.

Air, Water, and Food, from a Sanitary Standpoint. By Ellen H. Richards and Alpheus G. Woodman, Instructors in Sanitary Chemistry in Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall. 1900. 225 pp. Price, $2.00.

The Volatile Oils. By E. Gildemeister and Fr. Hoffmann. Translated

[1] This Journal, 21, 27.

by Edward Kremers. viii + 733 pp. Four maps and numerous illustrations. 1900. Milwaukee: Pharmaceutical Review Publishing Co. Price, $5.00 net.

The Wellcome Chemical Research Laboratories, Established 1896. By Frederick B. Power, Ph.D., Director, 6 King St., Snow Hill, London, E. C. 18 pp.

The Question of Temperature-Influence on the Specific Rotation of Sucrose. By Ferdinand G. Wiechmann, Ph.D. 1900. 37 pp.

Nutrition Investigations at the California Agricultural Experiment Station, 1896–1898. By M. E. Jaffa, M.S. Bulletin No. 84. U. S. Department of Agriculture, Washington, D. C. 39 pp.

A Report of Investigations on the Digestibility and Nutritive Value of Bread. By Chas. D. Woods and L. H. Merrill, Maine Agricultural Experiment Station. Bulletin No. 85. U. S. Department of Agriculture, Washington, D. C. 1900. 51 pp.

Commercial Fertilizers. By H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. Special Bulletin. August, 1900. 24 pp. Published by the author.

Elements of Mineralogy, Crystallography, and Blowpipe Analysis, from a Practical Standpoint, including a description of all common or useful minerals, the tests necessary for their identification, the recognition and measurement of their crystals, and a concise statement of their uses in the arts. By Alfred J. Moses, E.M., Ph.D., Professor of Mineralogy, Columbia University, and Charles Lathrop Parsons, B.S., Professor of General and Analytical Chemistry, New Hampshire College. New enlarged edition. viii + 414 pp., with 664 figures. New York: D. Van Nostrand Co. 1900. Price, $2.00.

The Elements of Physics for Use in High Schools. By Henry Crew, Ph.D., Professor of Physics in Northwestern University. Second Edition, revised. New York: The Macmillan Co. 1900. xvi + 353 pp. Price, $1.10.

The Laramie Cement Plaster. By E. E. Slosson and R. B. Mondy. Published as part of the Tenth Annual Report of the Wyoming College of Agriculture and Mechanics. Laramie, Wy. 1900. 18 pp.

Alkali Studies, V. By B. C. Buffum and E. E. Slosson. Published as part of the Tenth Annual Report of the Wyoming Experiment Station. Laramie, Wy. July, 1900.

Medical Legislation. Gov. Thomas' Veto of the Colorado Medical Bill. The Love Medical Bill of Ohio. Medical Ethics. Medical Talk Publishing Co., Columbus, Ohio. 16 pp. Price, 5 cents.

Bulletin No. 88. Commercial Fertilizers. August, 1900. 50 pp. Bulletin No. 89. Wheat. September, 1900. 24 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky.